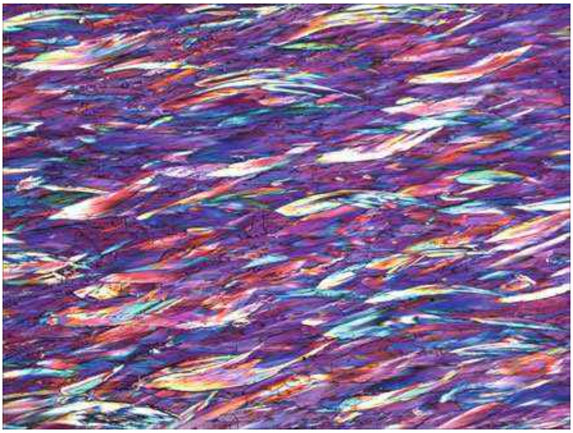
Kenyon Evans-Nguyen
Katherine Hutches *Editors*

Forensic Analysis of Fire Debris and Explosives

Springer

Forensic Analysis of Fire Debris and Explosives



‘School of fish’: recrystallized TNT viewed by PLM. Image courtesy of Brittany Crane Calhoun, Jamie Baerncopf, and Katherine Hutches of ATF

Kenyon Evans-Nguyen · Katherine Hutches
Editors

Forensic Analysis of Fire Debris and Explosives

Springer

Editors
Kenyon Evans-Nguyen
University of Tampa
Tampa, FL, USA

Katherine Hutches
Bureau of Alcohol, Tobacco, Firearms
and Explosives
Walnut Creek, CA, USA

ISBN 978-3-030-25833-7 ISBN 978-3-030-25834-4 (eBook)
https://doi.org/10.1007/978-3-030-25834-4

© Springer Nature Switzerland AG 2019
The chapter by Hazel Hutson is subject to Crown Copyright
This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Contents

1 **An Introduction to Instrumentation Used in Fire Debris and Explosive Analysis** 1
Kenyon Evans-Nguyen

2 **Introduction to Fire Debris Analysis** 45
Jamie Baerncopf and Sherrie Thomas

3 **Background Interference in Fire Debris Analysis** 75
P. Mark L. Sandercock

4 **Vegetable Oil, Biodiesel and Ethanol Alternative Fuels** 105
Douglas Byron

5 **Variation Within Ignitable Liquid Classes** 135
Mary R. Williams and Susan Seebode Hetzel

6 **Microbial Degradation of Ignitable Liquids** 175
Katherine Hutches

7 **Introduction to the Forensic Analysis of Intact Explosives** 193
H. E. Hutson and E. McGee

8 **Explosive Analysis: Introduction to Post-Blast Analysis** 227
B. M. Crane Calhoun and R. F. Mothershead II

9 **Explosive Device Componentry and Evaluation** 257
Kirk Yeager and John Jermain

10 **Bridging Explosives and Fire Debris Analyses** 285
Michelle Evans

11 Interacting with Other Disciplines 305
Carl E. Chasteen

Appendix A: Acronyms and Abbreviations 337

Appendix B: Answers to Chapter Questions 341

Editors and Contributors

About the Editors

Kenyon Evans-Nguyen is Associate Professor and Director of the Forensic Science Program at The University of Tampa. He publishes in forensic chemistry, specifically in the development of new technologies and methods in forensic mass spectrometry.

Dr. Katherine Hutches was a forensic chemist in the Bureau of Alcohol, Tobacco, Firearms, and Explosives until her departure in the summer of 2019. She specialized in fire debris and explosive analysis, and her published research topics include novel analytical methods, gasoline-chlorinator mixtures, and microbial degradation in moldy building materials.

Contributors

Jamie Baerncopf Bureau of Alcohol, Tobacco, Firearms and Explosives- Forensic Science Laboratory, Walnut Creek, CA, USA

Douglas Byron Forensic and Scientific Testing, Inc. (FAST Inc.), Lawrenceville, GA, USA

Carl E. Chasteen Division of Investigative and Forensic Services, Department of Financial Services, Bureau of Forensic Services, Havana, FL, USA

B. M. Crane Calhoun Bureau of Alcohol, Tobacco, Firearms and Explosives-Forensic Science Laboratory, Walnut Creek, CA, USA

Michelle Evans Bureau of Alcohol, Tobacco, Firearms and Explosives, Ammendale, MD, USA

Kenyon Evans-Nguyen The University of Tampa, Tampa, FL, USA

Susan Seebode Hetzel S-E-A Ltd, Columbus, OH, USA

Katherine Hutches Bureau of Alcohol, Tobacco, Firearms and Explosives, Walnut Creek, CA, USA

H. E. Hutson Defence Science and Technology Laboratory, Salisbury, Wiltshire, UK

John Jermain Bureau of Alcohol, Tobacco, Firearms and Explosives, Huntsville, AL, USA

E. McGee Centre of Forensic Sciences, Toronto, ON, Canada

R. F. Mothershead II Federal Bureau of Investigation Laboratory, Quantico, VA, USA

P. Mark L. Sandercock Retired, Royal Canadian Mounted Police, Edmonton, AB, Canada

Sherrie Thomas Bureau of Alcohol, Tobacco, Firearms and Explosives- Forensic Science Laboratory, Atlanta, CA, USA

Mary R. Williams National Center for Forensic Science, University of Central Florida, Orlando, FL, USA

Kirk Yeager Federal Bureau of Investigation, Quantico, VA, USA

Chapter 1
An Introduction to Instrumentation Used in Fire Debris and Explosive Analysis

Kenyon Evans-Nguyen

Learning Objectives

- Introduce basic principles for instrumentation commonly used in fire debris and explosive analysis.
- Understand the criteria for choosing the instrumentation that is the best fit for the purpose of specific analyses.

1.1 Background

The major focus of forensic chemists is to answer the question "What is this unknown material?" In fire debris and explosive analysis, the forensic chemist is typically attempting to identify an ignitable liquid or explosive material. Modern analytical instruments are the primary tools used to answer this question. Representations of forensic science in popular culture tend to significantly understate the work and expertise associated with obtaining usable data from instrumentation and overstate the ease of interpreting the subsequent data. Forensic instrumentation requires significant training to operate properly and to understand the data the instruments can produce. Forensic chemists train in standard operating procedures (SOPs) for using instrumental methods when they are initially hired, building from their academic science education. While whole books are written for each of the techniques that will be discussed, this chapter will provide a brief overview of instrumentation commonly used in fire debris and explosive analysis. Subsequent chapters will provide more detail about sample preparation methods specific to each type of fire debris and explosive evidence discussed.

K. Evans-Nguyen (✉)
The University of Tampa, Tampa, FL, USA

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_1

Before doing any analysis, the forensic chemist must decide what type of instrumental method to use. Even when the technique to be used is dictated by laboratory SOPs, it is still important for the scientist doing the analysis to understand why that method is a good fit for that purpose. For example, some instruments give elemental information, while others can potentially give molecular information. Each of these is useful, but the examiner must understand which technique or combination of techniques will provide the information that is necessary for the particular sample at hand.

Analytical methods are generally classified as qualitative or quantitative. Determination of the identity of a substance is a **qualitative analysis**. This is in contrast to quantitative analysis, which is a determination of the concentration of a compound after the identity is known. Quantitative analysis is central to forensic toxicology and some other forensic disciplines, but the analysis of fire debris and explosives is primarily qualitative analysis. One of the most important scientific criteria in qualitative analysis is selectivity. Selectively is how well a technique can distinguish between closely related compounds [1, 2]. Stated differently, it is how unique the signal generated from a technique is to a specific compound; the more compounds that can yield the same signal for a technique, the less selective the technique. Presumptive, or **screening**, tests are low sensitivity techniques that are often employed on scene or in the laboratory. These tests, such as color tests or ignition susceptibility tests, are typically rapid, simple tests, but give the same or similar result to a large range of chemical compounds. There are over 140 million known organic and inorganic compounds [3, 4]; screening tests can be useful in reducing that number of all possible compounds to a list of tens or hundreds of compounds. They may be used by law enforcement to provide probable cause in an investigation, help ascertain the safety of an unknown material found at a scene, or help an examiner determine an appropriate analysis scheme. However, the results of a screening test alone are not reliable enough to use in court testimony. As such, **definitive** or **confirmatory** tests are needed. Definitive tests rely on instrumentation for unambiguous identifications. Examples of such tests include mass spectrometry and X-ray diffraction. Some instrumental methods, including chromatography, are more selective than screening tests, but are not sufficient for identification. Identifications based on such data are often described as preliminary identifications. To obtain unambiguous identifications appropriate for use in court testimony, multiple techniques are used on the sample, such as pairing gas chromatography with mass spectrometry or combining the results of multiple preliminary methods.

Instruments must be used under appropriate conditions with the compound of interest, the **analyte**, in an appropriate state (solid, pure liquid, gas, solution) for reliable identification (Table 1.1). Another important consideration when selecting instrumentation for analysis of solutions is the **working range**. The working range is the range of concentrations between what will yield the lowest acceptable signal levels (often three times the signal-to-noise ratio) and what is so high that it distorts the signal; large working ranges are desirable. For qualitative analysis, the concentration of the sample is only significant in that it needs to be within the working range. While too little sample will yield an instrument response that falls below

Table 1.1 Synopsis of sample requirements for common instrumentation used in analysis of fire debris and explosives

Technique	Sample state	Type of identification	Other considerations/notes
High-performance liquid chromatography (HPLC)	Solution	Preliminary	Assuming a UV detector is used
Gas chromatography/flame ionization detector (GC-FID)	Solution, gas	Preliminary	No aqueous solvents
Gas chromatography/electron capture detector (GC-ECD)	Solution, gas	Preliminary	Selective for specific functional groups
Ion chromatography (IC)	Solution	Preliminary	Assuming a conductivity detector was used; when paired with MS detector, considered definitive for a given ion
Capillary electrophoresis (CE)	Solution	Preliminary	
Gas chromatography/mass spectrometry (GC-MS)	Solution, gas	Definitive	Detectable concentration range and resolution depend on ion source and type of mass analyzer
Liquid chromatography/mass spectrometry (LC-MS)	Solution	Preliminary/ definitive	
Attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FTIR)	Liquid, solid	Definitive	Solutions can be analyzed by allowing the solvent to dry
Raman	Solution, liquid, solid	Definitive	
X-ray fluorescence (XRF)	Solid	Preliminary/ definitive	Unambiguous elemental analysis; definitive for ID of pure elements
X-ray diffraction (XRD)	Solid	Definitive	Solid is ground to fine powder
Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS)	Solid	Preliminary/ definitive	Unambiguous elemental analysis; definitive for ID of pure elements

acceptable levels (as defined in the SOP), too much sample distorts the signal in some instruments. Additionally, too much sample can contaminate or damage sensitive instrumentation, requiring that the instrument be taken off-line for cleaning and repairs. Contamination is unacceptable in a forensic laboratory, and when it occurs, work on the affected instruments stops until the issue is resolved.

Beyond the scientific criteria discussed, there are important practical criteria to consider including cost, analysis time, convenience, and required skill of the operator. Nuclear magnetic resonance (NMR) is an example of a definitive technique that is widely used in other fields, especially organic chemistry, and rarely used in forensic chemistry. The selectivity of NMR is excellent, and the working range is acceptable for most forensic analysis. However, NMR is not easily automated, which increases overall analysis time and is less convenient. Further, the instrument requires significant maintenance of the cryogenic system and highly trained operators. This example is not meant to denigrate NMR, a powerful analytical technique, but to demonstrate that practical considerations are especially important in forensic chemistry, even in comparison with other fields of analytical chemistry.

1.2 Chromatographic Instrumentation

1.2.1 Theory of Chromatography

At the core of chromatography is the separation of the components of a mixture from each other. The most common chromatographic techniques used in fire debris and explosive analysis are liquid, gas, and ion chromatography. These chromatographic techniques are column-based; separations are achieved through differential retention of compounds on the column substrate. The **stationary phase** coats the interior of the column or is packed in the column and interacts with the components of a sample. The **mobile phase**, which may be either a solvent (e.g., LC, IC, and CE) or gas (GC), is used to push the sample through the column. During analysis, the components of a sample mixture may interact either with the stationary phase or with the mobile phase. The result of a chromatographic analysis is a chromatogram, where the x-axis is time, the y-axis is abundance, and components of a mixture are represented as peaks. The time between a compound entering a column and fully leaving the column, or eluting, is known as the **retention time** (t_r). If a compound has no interaction with the stationary phase, it is said to be **unretained** and will elute quickly after injecting onto the column. When an analyte of interest is unretained in a chromatography system, that system is likely inappropriate for analysis of that analyte. For example, liquid chromatography (LC) analyses typically use differences in polarity as the basis for separation; the stationary phase is often nonpolar with a polar solvent as the mobile phase. Most organic compounds will have some interaction with the column and be separated. However, ionic species such as nitrate and perchlorate have no interaction with a nonpolar column and are unretained.

If the experimental conditions are carefully controlled, the retention time is highly reproducible. When the examiner suspects that a sample contains a certain compound, they will run a known standard for that compound and the sample under the same conditions. If the retention times for the peak in the standard and the sample are consistent, the compound can be preliminarily identified. Identification based on retention times in chromatography is only preliminary; chromatography is not selective enough to be definitive. However, chromatography can be coupled with definitive techniques, such as mass spectrometry, to yield powerful hybrid instrumentation.

To achieve separation in chromatography, each component should have some affinity for the stationary phase, but the affinities for each component should differ,

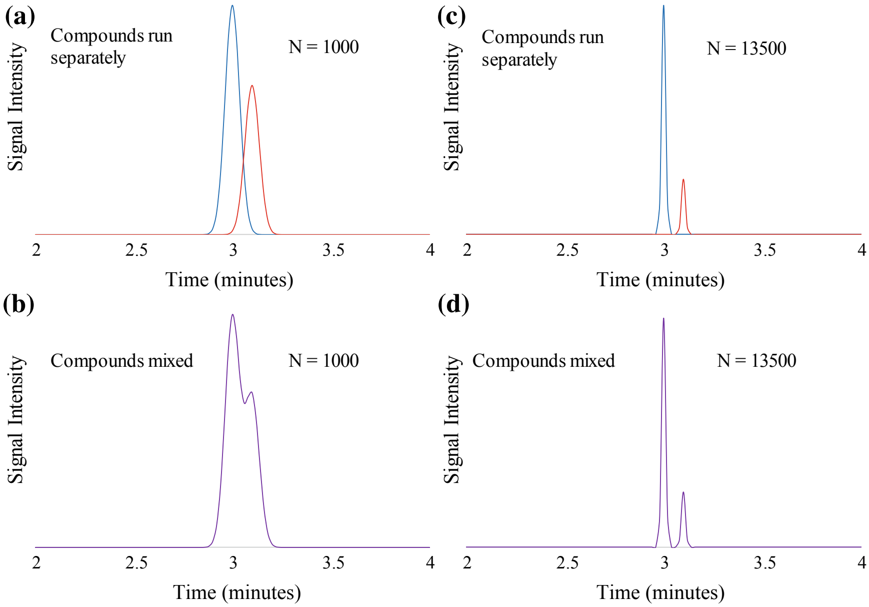


Fig. 1.1 Simulated chromatographic analyses of two compounds that elute close to each other run separately (**a**, **c**) and as a mixture of the two compounds (**b**, **d**). The analyses are simulated at a low plate count (**a**, **b**) and a higher plate count (**c**, **d**)

resulting in a separate peak for each component of the mixture. **Resolution** describes how well two components are separated, as illustrated in Fig. 1.1. When two compounds are not adequately separated (Fig. 1.1b), the compounds are **unresolved**. In this case, the analyst is unable to identify each component without deconvolution or background subtraction, lessening confidence in the identification. When the signal intensity returns to baseline between the two peaks (as in Fig. 1.1d), the peaks have achieved **baseline resolution**. For complex mixtures, including most petroleum-based ignitable liquids, it is difficult to achieve baseline separation for all components in the mixture. However, conclusions can still be drawn about the composition of the sample by combining the information obtained from the chromatogram with the information contained from the mass spectrometer in a GC-MS instrument.

Chromatographic resolution changes when the mobile or stationary phases are changed. When confronted with problematic unresolved compounds, one solution is to experiment with different columns until acceptable resolution is achieved. In liquid chromatography, changing the mobile phase composition is another common approach. Temperature programming in gas chromatography or a mobile phase gradient in liquid chromatography can also be used to change compound retention and improve resolution.

The primary metric to measure the effectiveness of separations is the **theoretical plate (N)**. Analogous to using horsepower as a measurement of power in engines, the name "theoretical plate" has historical origins that are now largely outdated. The term is rooted in fractional distillation, where gas-phase mixtures are separated by condensation on plates. The more plates that are used in a distillation column, or the more theoretical plates in a column chromatography separation, the better the separation. Figure 1.1 illustrates the effect of increasing plate count in a separation. When a mixture of the two closely eluting compounds is analyzed at a lower plate count (Fig. 1.1b), they cannot be effectively separated. At a higher plate count (Fig. 1.1d), the compounds can be clearly differentiated. Though there are several ways to increase the value of N and thereby increase the efficiency of a separation, the two main ways that an examiner can affect separation efficiency are by increasing the column length and optimizing the flow rate to decrease **band broadening**.

Separation efficiency is often measured as **plate height (H)**, which is sometimes referred to as height equivalent to theoretical plate (HETP). Plate height expresses the length of column needed to achieve one theoretical plate and can be expressed as $H = \frac{L}{N}$, where L is column length. The units of H are usually given in centimeters or millimeters. Using LC as an example, typical commercial instrumentation can be expected to achieve 5000–40,000 theoretical plates, with plate heights of 0.2–0.03 cm [5]. In extreme experimental instruments, as many as 500,000 theoretical plates have been achieved, with a plate height of 0.0002 cm [6]. Plate height represents efficiency of the separation, which is a function of band broadening. Band broadening is illustrated in Fig. 1.2. When a mixture is injected into a column, not only do the different components separate into bands, but the bands of each component spread out. This results in wider peaks and reduced resolution.

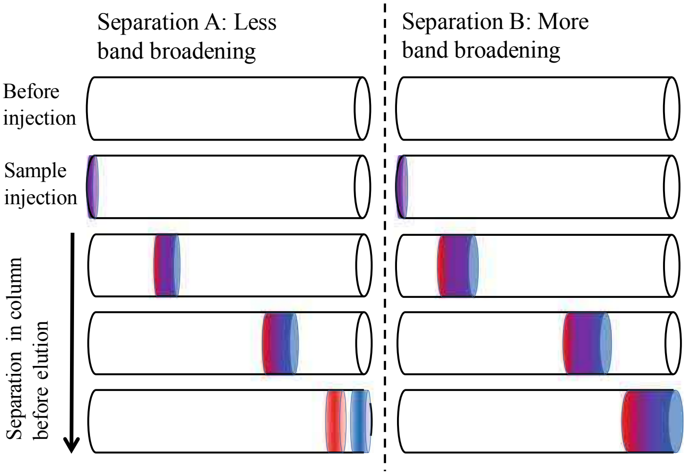

Separation A: Less band broadening
Separation B: More band broadening
Before injection
Sample injection
Separation in column before elution

Fig. 1.2 Illustration of band broadening

Separation b in Fig. 1.2b undergoes significant band broadening and results in unresolved peaks. As band broadening is minimized, more efficient separation and lower plate heights can be achieved.

Band broadening is caused by three primary factors: multiple path lengths, diffusion, and equilibration times. The multiple path length contribution is most significant in packed columns. For the capillary columns used in GC, this factor is essentially negligible. Diffusion is inherent spreading of peaks due to random thermal motion. Broadening due to diffusion is minimized by using high flow rates of mobile phase through the column which also decreases analysis time. Band broadening from the equilibrium time, also known as mass transfer, results from the non-equilibrium nature of chromatography. Molecules in samples injected into the column are in motion throughout the experiment and are not allowed time to achieve a true equilibrium between the stationary phase and the mobile phase. Allowing more time for equilibration by reducing the flow rate through the column minimizes broadening due to this factor, though it increases the analysis time and increases broadening due to diffusion. For each chromatographic system, there will be an optimum flow rate that minimizes the plate height and yields the least band broadening. Analysis time, as well as the limitations of the pump and hardware, should also be considered in deciding the flow rate. Most forensic laboratories will rely on previously determined methods that have proven efficiency and resolution with reasonable analysis time.

1.2.2 Liquid Chromatography

There are numerous variations of the term **liquid chromatography** (LC) in common use (see inset), but the principle of the technique is the same. Liquid chromatography is primarily used for organic compounds, exploiting differences in polarities of compounds to effect separation.

Liquid chromatography allows for the analysis of compounds with thermally labile bonds or compounds that do not readily volatilize, which includes many organic explosives such as triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD). Liquid chromatography can be performed at ambient or slightly elevated temperatures; thermally labile compounds are less likely to degrade in these more moderate temperatures than in the higher temperatures used for other techniques. While LC is commonly used in the analysis of organic explosives, it is rarely used in the analysis of ignitable liquids. Common LC detectors are largely insensitive to aliphatic hydrocarbons, which are major components of most ignitable liquids.

Terminology in commercial liquid chromatography systems

When pumps were originally used to apply pressure to the mobile phase in LC, the technique was termed high-pressure liquid chromatography (HPLC).

Soon, the use of pumps became commonplace and what were formerly considered “high” pressures were now normal pressures, so the acronym HPLC was revised to be high-performance liquid chromatography.

In recent years, developments in column technology and improved pump engineering have resulted in even higher-pressure systems; the pumps, tubing, and fittings for these instruments can function at the much higher pressures required for newer columns. These have been given a variety of acronyms by the companies commercializing the systems, but are most often called ultra-high-pressure liquid chromatography (UPLC or UHPLC). Further, when an HPLC or UPLC system is connected to a mass spectrometer, the “HP” or “UP” is dropped from the acronym and the system is simply called an LC-MS. These often confusing variations in terminology are usually done for commercial reasons and do not reflect significant variations in the science occurring.

A typical modern instrument used for LC is illustrated in Fig. 1.3. This system is represented as a binary system with two solvents and two pump heads. Most commercial systems are actually quaternary, capable of pumping four solvents. While only two solvents are generally used during chromatographic runs, the other two solvents can be used for automated rinse and cleaning processes. By

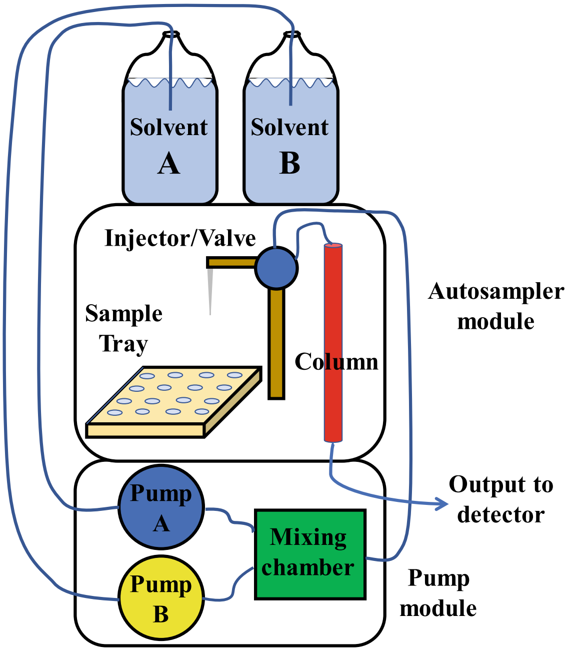


Fig. 1.3 Schematic of a liquid chromatography system

convention, solvent A is typically an aqueous solvent and solvent B is organic solvent, often methanol or acetonitrile. The multiple solvents, multiple pump heads, and mixing chamber allow the chromatographic solvent to be altered rapidly and simply with the software.

To inject the sample, the injector needle pierces the sample vial septum and draws out a set amount of sample (typically 1–20 μL) into a short length of tubing, known as the injection loop. The valve in the injector is positioned so the solvent is pumped through the valve, into the column, and to the detector but bypasses the injection loop. The detector begins to collect data when the valve switches positions, causing the solvent to flow through the injection loop, pushing the loaded sample onto the column [7].

The most commonly used type of stationary phase in LC is a "**reversed-phase**" packed column, meaning that the column is a tube packed with nonpolar, homogenous, small (1–10 μm) particles. The homogeneity of the particles is critical to separation efficiency. Smaller particles (<3 μm) yield better separations and faster run times, but the pressure required by the pumps to run the solvent at typical flow rates (0.3–2 mL/min) dramatically increases as particle size is decreased. Silica is a cheap and abundant material that was originally used as the column packing in liquid chromatography; it is still commonly used in crude separations in organic laboratories meant to clean up synthesis products. However, bare silica is not reliable enough for analytical separations and, because the surface is highly polar, it does not retain most organic compounds well. In most modern analytical LC separations, including those used for explosive analysis, the silica substrate is coated with a nonpolar compound, "reversing" its phase from polar to nonpolar. The most commonly used coating converts the silica surface to an octadecane (C18) surface.

An aqueous solvent can be used with a nonpolar stationary phase such as a C18 column to provide a stark contrast in polarities. In such a system, polar compounds will have high affinity for the aqueous mobile phase and little affinity for the stationary phase, resulting in minimal retention and rapid elution. Strongly, nonpolar compounds will be highly retained and elute slowly, resulting in poor peak shapes. By using a less polar organic solvent as a second component of the mobile phase, the mobile phase composition can be tuned to elute compounds in a reasonable time with acceptable peak shapes. In an analysis of a sample with only one primary component or a mixture of a few compounds with similar polarities, using a fixed mixture of the aqueous and organic mobile phases throughout the analysis tends to yield the most efficient and timely separations. In mixtures containing compounds with significantly different polarities, a gradient separation is necessary. In this case, the analysis starts with a mixture containing primarily aqueous mobile phase (e.g., 95% aqueous and 5% organic) and the composition of the mobile phase mixture is changed linearly over time during the separation to a high organic composition (e.g., 10% aqueous and 90% organic). In a gradient separation, weakly retained compounds can experience some retention at the initial low organic mobile phase mixture but more nonpolar compounds are still eluted effectively in the same run by the final high organic mobile phase mixture.

Compounds that are too polar or ionic are not easily analyzed in reversed-phase LC even when the mobile phase composition is changed. Polar columns can be used for the polar organic compounds (e.g., sugars); however, few polar compounds are routinely of interest in explosive or fire debris analysis. Ions, however, are an important class of analyte in explosive analysis. Ion chromatography or capillary electrophoresis is more suitable for the analysis of ions than LC and will be discussed in a subsequent section.

The detector used in a chromatographic experiment is critical and largely determines the selectivity and sensitivity of the analysis. Retention times provide some information about the identity of the compound and can be used as a presumptive test, but further information from the detector is required for a definitive identification. In forensic science laboratories, ultraviolet spectrophotometer (UVS) and mass spectrometer are the most commonly used LC detectors. Ultraviolet spectrophotometry is based on absorbance of light by electrons, which will be discussed further in Sect. 1.4.1.

A UV spectrophotometer consists of a UV light source, a sample cell, and a detector. **Photodiode arrays** (PDAs), also called diode array detectors (DADs), are the most common type of detector for a spectrophotometer to be used as an LC detector. The photodiode does not determine the specific wavelength (energy) of light, but it generates a voltage proportional to the intensity of the light. Wavelength discrimination must be included elsewhere in the instrument design of the spectrophotometer. Figure 1.4 shows an LC detector that uses a diffraction grating coupled with a PDA to detect all wavelengths in the spectrum rapidly as samples elute.

The light from the source impinges on the sample, and the light that is not absorbed is spatially separated into its constituent wavelengths by the diffraction grating. An array of individual photodiodes measures the intensity of light transmitted through the sample (transmittance) for each wavelength of light. Absorbance results in a decrease in the intensity of the transmitted light and a decrease in

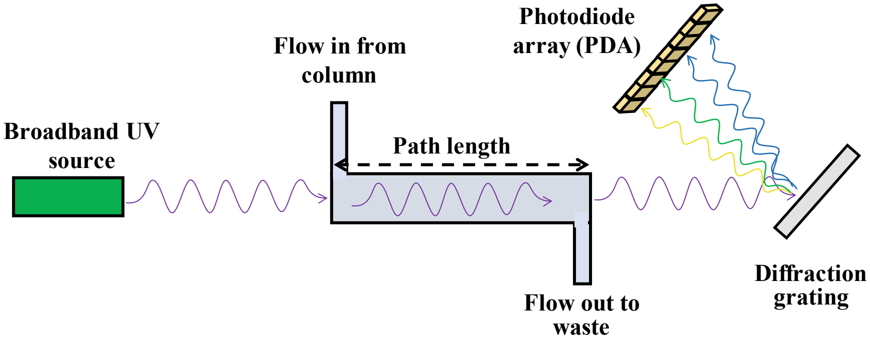


Fig. 1.4 Schematic of a UV spectrophotometer for use as an LC detector

voltage at the detector. Transmittance is readily converted to absorbance through the following equation:

$$A = 2 - \log(\%T)$$

where A is absorbance (a unitless measure) and %T is percent transmittance. In UV spectrophotometry, viewing signal in terms of absorbance is preferable because absorbance is directly proportional to sample concentration [8]. Ultraviolet detectors are reliable for precision quantitation, and LC with a UV detector is commonly used for this purpose.

The mobile phase in an LC experiment with a UV detector should be chosen such that UV absorbance is minimal. If the mobile phase itself absorbs in the UV region of interest, the detector background will be too high for effective analysis. Most organic compounds absorb ultraviolet light, so UV detectors can detect a wide range of organic compounds. Mass spectrometer is a powerful detector that is often coupled with LC and will be discussed further in Sect. 1.3. However, most of the aliphatic hydrocarbons that are important in the analysis of fire debris do not absorb in the UV region and are not easily analyzed with LC-MS. While LC is useful for explosives that are nonvolatile or thermally labile, it has limited use for fire debris.

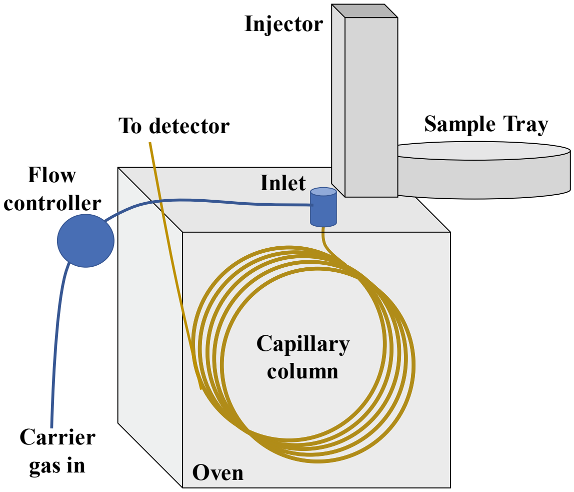
1.2.3 Gas Chromatography

Gas chromatography (GC) is one of the most widely used analytical techniques throughout industrial and forensic laboratories today. It is also the central technique in the analysis of fire debris evidence as it couples well with headspace analysis. Advantages of GC include fast analysis times, high resolution, good sensitivity, high reliability, and relatively low cost. The primary disadvantage is that it relies on conversion of the sample to a gas. Compounds which are not sufficiently volatile can be derivatized to improve vaporization and stability, but this is a labor-intensive sample preparation step [9]. Thermally labile compounds, including many explosives, have to be analyzed under carefully prescribed conditions with GC to prevent degradation of the compound in the inlet or during the separation [10].

A GC consists primarily of an injector, an inlet, and a temperature-programmable oven containing a column, as shown in Fig. 1.5. As with LC, GC instruments in forensic laboratories are normally equipped with an autosampler, which enhances reproducibility and throughput. Samples for GC analysis should be dissolved in an appropriate solvent, except in the headspace analysis. Solvents are often small, highly volatile compounds such as methanol, carbon disulfide, or dichloromethane, which are not retained on the column.

The GC columns used in modern forensic science are not packed tubular columns, but are very narrow diameter (usually 250 μm) capillary columns with a thin coating of stationary phase on the interior of the column. Because the columns are open capillaries and the mobile phase is a gas (as opposed to the much more viscous

Fig. 1.5 Schematic of a gas chromatography system



liquids in LC), very long columns can be used without incurring problematic backpressures. Column lengths of 6–30 m are typical, resulting in a high number of theoretical plates and efficient separation. In the analysis of the highly complex mixtures inherent to fire debris samples, separation efficiency is paramount. The columns are based on fused silica substrates, with a protective coating of polyimide on the outside to prevent cracking or breaking. The interior surface of the column is coated with a thin layer of a polymer that imparts the stationary phase chemistry. The most common stationary phases are based on polydimethylsiloxane (PDMS), which yields a nonpolar stationary phase consisting of exposed methyl groups. Phenyl groups can be mixed into the methyl stationary phase in controlled proportions to adjust polarity. A common stationary phase consists of a coating that is 95% methyl/5% phenyl where 5% of the functional groups at the surface are phenyl groups interspersed among the majority of methyl groups. Columns that are 50% methyl/50% phenyl are also common [11].

One major difference between GC experiments and LC experiments is the role of the mobile phase. Separations in LC exploit differences in analyte affinity for the mobile and stationary phases, and the mobile phase is often varied during analysis. In GC, the mobile phase is a highly pure inert **carrier gas** (usually He, N_2, or H_2). Gas mixtures are not used, and the gas composition is not varied. Compounds in GC analysis do not experience a particular affinity for the carrier gas, but are retained as a result of an affinity for the stationary phase. The retention time of a compound in GC is based on a convolution of its affinity for the stationary phase and its volatility. The carrier gas serves only to propel the compound through the column, while it is in the gaseous state and not adsorbed onto the column surface. The choice of carrier gas does influence separation efficiency. Helium and hydrogen both facilitate more efficient separation than nitrogen. Helium was traditionally the preferred carrier gas, primarily because of safety concerns with the use of hydrogen gas. However, helium is a non-renewable resource and as helium reserves have dwindled in recent years, the price of the gas has increased substantially. As such, some laboratories have adopted hydrogen generators which allow hydrogen to be used safely as a carrier gas.

A small volume (1–5 µL) of sample is injected into the heated (150–350 °C) inlet, where it vaporizes at the elevated temperature. To preserve separation efficiency, the volatized gas sample is split by the carrier gas flow, such that some of the sample is introduced into the head of the column while much of the sample is diverted out of the inlet to the surrounding atmosphere. **Split ratios** (the ratio of gas flow diverted out of the inlet to the gas flow directed onto the column) of 10:1–50:1 are common, so most of the injected sample does not reach the column but is vented out of the inlet. Low split ratios, or splitless injections, are generally used in circumstances where high sensitivity is needed and potentially wider peaks with poor peak shapes are acceptable.

Temperature in GC is analogous to mobile phase composition in LC. Careful temperature control is maintained by the oven, which contains the column. When the oven is held at a high temperature, compounds tend to elute faster. Just as the solvent ratios in LC can be adjusted to maximize separation efficiency, temperature programs can be used to more efficiently separate complex mixtures of compounds by GC while maintaining good peak shapes. A program will start and hold at a lower temperature. Smaller, more volatile, more polar analytes (assuming a nonpolar column is used) will elute first. As the temperature ramps up, larger, less volatile, more nonpolar compounds can elute. In complex mixtures encountered in fire debris analysis, use of an appropriate temperature program is essential to obtaining useful data.

There are a myriad of detectors that can be coupled with GC, but the most commonly used detector in fire debris and explosive analysis is a mass spectrometer. Gas chromatography coupled with a mass spectrometer (GC-MS) will be discussed in more detail in Sect. 1.3.6. The flame ionization detector (FID) is a near-universal detector that is used by some laboratories for fire debris analysis, typically in conjunction with an MS detector, and is also widely used in forensic drug chemistry screening. The FID integrates a flame at the end of the column and a detector to measure ion current. As compounds elute from the column and undergo combustion in the flame, the ions generated are measured as a current yielding a signal proportional to the amount of the compound. An FID can detect nearly any carbon-containing compound but is not selective. A GC-FID instrument only yields retention times with no molecular information, severely limiting the utility of this detector for analysis of complex mixtures, including fire debris evidence and post-blast explosive samples.

Several GC detectors are capable of selective detection of organic explosives, including the electron capture detector (ECD) and chemiluminescence/thermal energy analyzer (TEA). The ECD consists of a radioactive film that emits a near-constant current of electrons (β emission). The current is monitored, and if a compound elutes that can undergo electron capture, the number of electrons hitting the anode is reduced and the current decreases. These current dips yield the signal for the sample. Most compounds are not capable of efficient electron capture and remain undetected by the ECD. However, compounds with highly electronegative elements (Cl and F particularly) or functional groups (nitro groups) do undergo electron capture and yield signal in ECDs. ECDs are highly sensitive to organic nitro-based explosives and impart some selectivity in analysis [12, 13]. However, solvents must be chosen carefully, as dichloromethane, a common solvent for the extraction of explosives, will be readily seen by the ECD detector. Chemiluminescence analyzers are highly selective for nitrate esters, nitramines, and nitroaromatic compounds, making them well suited for analysis of many organic explosives in complex matrices. Compounds containing these functional groups are detected through a series of reactions starting with pyrolysis of the eluted compounds in a heated oven, in the presence of a catalyst. Any available nitroso (R–N=O) groups undergo degradation and are converted to nitric oxide in this environment. The nitric oxide is then exposed to ozone in a reaction cell, forming nitrogen dioxide in an excited state (NO_2*). When NO_2* relaxes to ground state NO_2, an infrared photon is emitted, which is detected by a photomultiplier tube. Although this series of reactions seems complex, they impart excellent selectivity for nitro-based organic explosives [14, 15].

1.2.4 Ion Chromatography

Many explosive mixtures and residues are based on the chemistry of salts composed of polyatomic ions including nitrate, nitrite, chlorate, perchlorate, and ammonium. Neither LC nor GC is well suited for analysis of such inorganic ions, but ion chromatography (IC) and capillary electrophoresis (CE) are capable in this regard. Because of its high sensitivity and selectivity, IC has become the primary analytical method for ions in explosives [16, 17]. Ion chromatography also couples well with mass spectrometry, which can yield definitive data [18, 19].

In practice, an IC will resemble an LC, with some important deviations. Separation is achieved using a tubular column packed with homogenous small particles. Ion exchange chromatography (IEC), a technique similar to IC, can be performed directly on LC instrumentation by using a charged stationary phase. However, the performance of IC for inorganic ions is enhanced over IEC on an LC instrument because IC instrumentation includes components for eluent suppression (discussed later in this section) [20].

Separation in IC is due to differences in electrostatic affinity, which are based on primary charge state and ionic radius. Most ions relevant to forensic science are singly charged, but they still separate from each other during the IC analysis based on ionic radius. Smaller ions are expected to have a higher affinity for the charged stationary phase. Importantly, ionic radius changes significantly for hydrated ions, relative to ions not in solution. For example, the ionic radius of lithium increases by a factor of $\sim 7\times$ when hydrated [21].

A stationary phase with a positively charged surface chemistry would be used for anion analysis. The mobile phase in IC is an ionic solution with a polarity that matches the analyte ions. For anion analysis, aqueous solutions of hydroxide (NaOH) and carbonate/bicarbonate (sodium or potassium salts) eluents are common. The anions in the mobile phase displace the analyte ions from the positively charged stationary phase so that they flow through the column and elute. Hydroxide ions have a low affinity for a positively charged stationary phase such that it is appropriate for analytes that are weakly bound to the column. The affinity of a carbonate/bicarbonate eluent for the stationary phase can be tuned by adjusting the ratio of the two ions in the mobile phase. In analysis of cations, the competing ion in the mobile phase is most commonly the hydronium ion, and its concentration is controlled using buffers that have a low affinity for the stationary phase, such as methanesulfonic acid [21]. As in LC, the eluent should be selected such that the ions in the sample are retained by the ionic column to some degree, but are effectively eluted in reasonable time with minimal band broadening.

The most commonly used detector in IC is the **conductivity detector**, a simple and elegant detector. Conductivity (the reciprocal of resistivity) is a commonly measured parameter throughout science and industry. Conductivity detectors for IC determine conductivity based on resistance of the solution. At room temperature, ultrapure water has a resistance of 18.15 MΩ/cm, which corresponds to a conductivity of 0.05508 µS/cm [22]. The presence of ions in water increases the conductivity. In the detector, a constant current is applied to the solution while the voltage drop is measured, and the resistance is determined through Ohm's law. Most conductivity detectors will include temperature measurements and account for variations in conductivity with temperature fluctuation [23]. Monitoring the conductivity of the eluent will yield peaks when ions elute.

Conductivity detectors are universal for ionic species and sensitive to small ions relevant to explosives, such as nitrate and perchlorate. The issue with ion separations using charged columns prior to the invention of IC was the background of anions in the mobile phase. Without proper consideration, the conductivity signal is overwhelmed by the high background of anions in the mobile phase and sensitivity to the analytes would be poor. Incorporation of eluent suppression in the 1970s was the breakthrough in ion chromatography that imparted the sensitivity and selectivity to make it the preferred method for inorganic explosives [24]. Ion suppression is achieved in a separate column after the analytical column. The high conductivity ions in the mobile phase are exchanged with low conductivity ions through ion exchange [25] or chemical reaction [26] in the suppressor. The net result is that the background noise from the mobile phase is suppressed and the analyte ions are detected with greatly enhanced sensitivity.

As in LC, UV detection can be used as most relevant anions have some absorbance in the ultraviolet range. Many polyatomic ions relevant to explosive analysis (nitrite, nitrate, chlorate, and perchlorate) absorb in the ultraviolet range and can be detected with a UV detector [24]. However, the performance of a UV detector for IC is poor in comparison with a conductivity detector combined with eluent suppression. Mass spectrometer is used extensively as a detector for IC, with an interface similar to LC-MS. As with conductivity, IC-MS performance is generally improved with the use of eluent suppression.

1.2.5 Capillary Electrophoresis

While IC is the most commonly used technique for analysis of ionic content in explosives, capillary electrophoresis (CE) is a useful alternative method. CE is quite versatile and can also be used for organic compounds or biomolecules in addition to ions. The major advantage of CE is the potential for very high-efficiency separations relative to LC or IC. CE requires little sample, so injection volumes are small and little solvent is consumed. However, only small injection volumes and sample amounts can be used to maintain adequate separation.

Capillary electrophoresis is not true chromatography in that it is not based on sample interactions with a mobile phase and stationary phase; there is no stationary phase in CE, and the flow of the solvent is not driven by a pump. A high voltage of 10–30 kV is applied to a narrow capillary (very similar to an uncoated GC capillary) between the solvent reservoir where the sample is injected and the capillary outlet. The capillary has a negatively charged surface such that positive ions in the solvent will preferentially congregate at the capillary wall. In the high electrical field, the positive charges attracted to the surface of the capillary wall migrate toward the negative charge at the capillary outlet. Because the capillary is narrow, this flow of ions at the surface creates a bulk flow (electroosmotic flow) which pushes the sample through the capillary. Analytes in the mixture will separate according to size and charge as they migrate through the capillary. Small, highly charged ions will migrate faster than heavier, singly charged ions. Detection at the capillary outlet can be accomplished through conductivity or mass spectrometry [10, 27].

1.3 Mass Spectrometry

1.3.1 Overview of Mass Spectrometry

Mass spectrometry (MS) is the most widely used detection technique in forensic chemistry. It is definitive and sensitive, and can be easily coupled to chromatography, particularly gas chromatography. The coupling of chromatography with MS is convenient for complex mixtures; the components of the mixture are separated by chromatography, and the resulting mass spectra are high-quality spectra for ideally pure samples. The confidence in definitive identification using FTIR, Raman, or XRD is reduced when working with mixtures. The quality of the spectra/diffractograms is reduced as the data is a convolution of all the components in the mixture.

Mass spectrometry is based on a fundamental property of matter: mass. It is a universal technique; all atoms or molecules have mass and can be detected with MS under the correct conditions. The MS techniques used in forensic chemistry are largely focused on identification of organic molecules, including hydrocarbons in

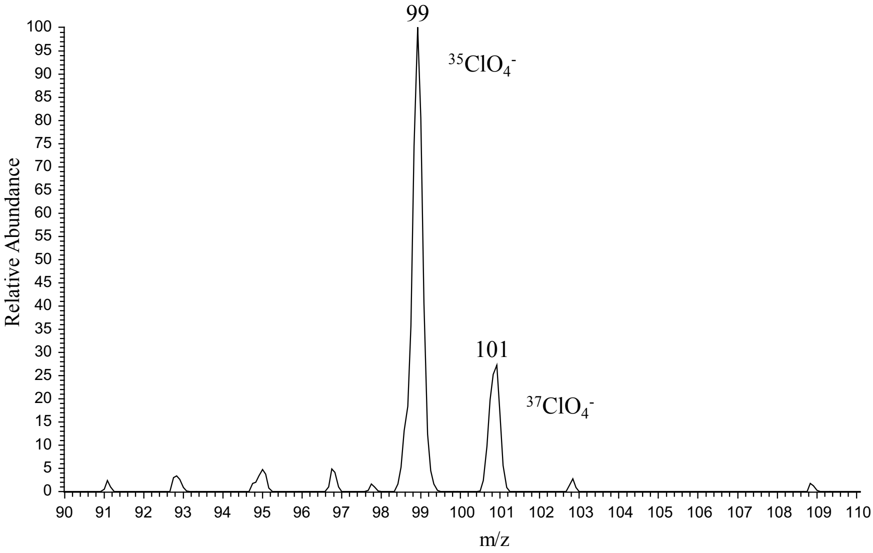


Fig. 1.6 A mass spectrum of perchlorate obtained using desorption electrospray ionization with an ion trap mass analyzer in negative mode

ignitable liquids and organic explosives. Mass spectrometry is also used for inorganic explosive components, often through its use as a detector for ion chromatography. The actual property measured in mass spectrometry is not mass, but **mass-to-charge ratio (*m/z*)**. A mass spectrum is a plot of intensity versus *m/z*, as shown in Fig. 1.6. For most of the analytes in forensic chemistry, the charge will be +1 or −1 such that, in practice, the peak observed in the spectrum usually corresponds directly to mass ($m/1 = m$). The *m/z* that corresponds to the singly charged intact analyte in the mass spectrum is known as the **molecular ion**, which is often a key to the identification of an analyte.

Figure 1.6 illustrates some important features of mass spectrometry. The molecular mass of ClO_4^- is 99 amu; therefore, the peak at *m/z* 99 corresponds to the molecular ion. Because chlorine has two isotopes, ^{35}Cl and ^{37}Cl, the spectrum has a second peak at *m/z* 101, corresponding to the molecular mass with the heavier isotope. Isotopes are apparent in mass spectrometry, and the isotopes of chlorine are especially noticeable [28].

A mass spectrometer consists of three main components: an **ion source**, **mass analyzer**, and detector. The ion source, as the name suggests, converts the sample into ions. The mass analyzer is the heart of the mass spectrometer, where ions are separated according to their mass-to-charge ratio (*m/z*). Combinations of constant voltages and varying voltages applied by electrodes with carefully designed geometries are used to manipulate the motion of the ions. For most mass analyzers, the ions collide with a detector after they are sorted by *m/z*. The detector converts the energy from the ion impact into a voltage which yields the signal intensity.

In some instruments (namely Orbitrap and ion cyclotron resonance instruments), the mass analyzer itself functions as the detector. Because gas-phase ions are unstable under ambient conditions, the mass spectrometer is kept under vacuum.

To call an instrument a “mass spectrometer” without further clarification is overly vague, similar to saying “mode of transport” when describing your car—you could be talking about a fighter jet or a tricycle. There are a myriad of different configurations of ion sources and mass analyzers, and many of them have very different functions. Mass spectrometer is very versatile; different mass spectrometer configurations can be used for analysis of organic compounds, inorganics, atomic spectra, or accurate isotopic analysis. Specifying the ion source and mass analyzer in the mass spectrometer clarifies the type of instrument being used. There are numerous different ion sources and mass analyzers. The following sections will focus on the small subset of ion sources and mass analyzers most commonly used in forensic chemistry.

1.3.2 Ion Sources

Analytes are converted to ions in the ion source. The feature that most differentiates various ion sources is the extent of **fragmentation** that occurs in the source. In the extreme, there are plasma sources that have temperatures on the order of the temperature of the sun. Compounds exposed to these sources are stripped to their atomic constituents. Many ion sources are “soft” ion sources and generate only yield intact ions that have not undergone fragmentation. Most soft ion sources produce protonated molecular ions, which have the mass of the ions plus the mass of the associated H^+ ion ($M + H^+$ ion). Ion sources that are considered “hard” are ion sources that generally cause fragmentation of a molecule without reducing the molecule in question to atoms.

Electron ionization (EI), formerly known as electron impact, is the “hard” ion source commonly used for analysis of organic compounds throughout analytical chemistry. It is also the most commonly used ion source in forensic chemistry that is coupled with GC-MS, particularly for fire debris analysis. The EI sources in commercial GC-MS instruments yield highly reproducible fragmentation, which is ideal for definitive identification. Some mass spectrometry methods are capable of imparting energy to the gas-phase ions in the instrument such that bonds are broken and the ion fragments. If the method is highly reproducible and there is a statistical population of ions, the spectrum of fragment ions formed is a definitive chemical “fingerprint.” Fragmentation can take place in the ion source concurrent with the initial ion formation (in-source fragmentation). The EI source has to be at reduced pressure to function, and so it is incorporated into the vacuum system with the mass analyzer [29]. Further, the sample must be introduced into the EI source as a gas. In GC-MS, the outlet of the column is positioned just outside of the EI source such that the eluting gaseous compounds are directly introduced into the source (Fig. 1.7). Ionization is accomplished with a beam of electrons generated by

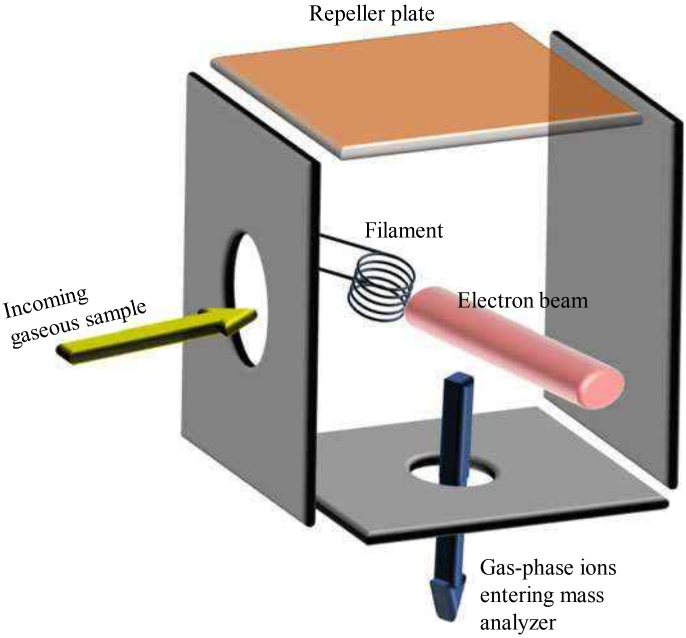


Fig. 1.7 Representation of an EI source

applying current to a metallic filament at a precisely controlled energy (generally ~70 eV). The incoming sample passes through the electron beam and can be ionized. A voltage is applied to the top of the EI source, also known as the repeller plate, to push ions formed in the source to the mass analyzer.

The 70 eV electrons in the beam can excite electrons associated with heteroatoms and in bonding orbitals of a given molecule with enough energy that they are ejected from the molecule, rendering it a radical cation. Radicals are quite unstable and will readily react with other molecules. In the reduced pressure of the EI source, most of the population of radical cations formed will undergo an internal reaction, rather than reacting with another molecule to form a more stable ion or to release a stable neutral. The result is an array of fragments which yields an information-rich spectrum containing numerous peaks [28]. For most compounds, there will be a peak for the ion corresponding to the intact molecule called the molecular ion (M^+) but most of the mass spectrum will be fragment ions. To use an EI spectrum for definitive analysis, the spectrum should be for a single compound. The coupling with gas chromatography functions as an online purification for each compound in the mixture prior to analysis in the EI source, assuming all peaks in the chromatogram are adequately resolved.

Maybe the most important advantage of the EI source in fire debris analysis is that it is a nearly universal source. Almost all organic compounds will ionize to some extent with EI, and it is the only ion source for which that is true. Many aliphatic hydrocarbons, particularly alkanes, ionize very poorly in nearly all ion sources, except for EI. GC-MS is the main technique used in fire debris analysis, and without EI, it would be difficult to analyze many ignitable liquids in any meaningful way using mass spectrometry.

Chemical ionization (CI) is closely related to the EI source in terms of the engineering of the instrument, but the chemistry that takes place in the source is very different [30, 31]. It is a much softer technique than EI, and while some limited fragmentation usually occurs, the most abundant peak is often the protonated molecule $[M + H]^+$. While mass spectrometers are most often set to detect positive ions (positive mode), nearly all commercial instruments can easily be set to detect negative ions instead (negative mode). Negative mode is quite effective when used with CI, with many compounds forming the deprotonated molecule $[M - H]^-$. Chemical ionization is particularly useful for compound with labile bonds, including most organic explosives. Such compounds are often highly fragmented in an EI source, such that the mass spectrum primarily consists of smaller fragment ions. The use of CI significantly reduces in-source fragmentation; a small number of high reactivity organic explosives may yield nearly intact fragment ions such as $[M - OH]^-$, $[M - NO]^-$, or $[M - NO_2]^-$ in negative mode, where they would only have small fragments in EI. With most commercial GC-MS instruments, a CI source is available as an add-on to the instrument and switching from EI to CI is as simple as checking a box in the instrument software. For explosives that are heavily fragmented in EI, switching to CI can yield data for the intact (or nearly intact) molecule and enhance confidence in identification. A drawback to using CI is the need for an in-house library, particularly for explosive analysis. The spectra in CI are highly dependent on the precise CI settings, such as the gas used and the voltage applied.

In CI, the same chamber as the EI source is used (Fig. 1.7). When the CI option is selected, a supplementary gas, called the reagent gas, is introduced into the chamber [32]. The amount of reagent gas added causes a minor rise in pressure in the source, but is large relative to the amount of gaseous sample entering the source. Because the source is flooded with reagent gas, the reagent gas is ionized in the electron beam instead of the analyte and the analyte is likely to react with ionized reagent gas. The radical cations formed from the reagent gas are surrounded by other molecules of reagent gas and react with them to form other ions. A cascade of reactions yields ions capable of more mild reactions than would take place in the EI source, such as proton transfer. The most commonly used reagent gas is methane, which can form reactive species and ionize the sample through the following reaction sequence:

$$\begin{aligned}
&\mathrm{CH_4} + \mathrm{e}^- \rightarrow \mathrm{CH_4^+} + 2\mathrm{e}^- \\
&\mathrm{CH_4^+} + \mathrm{CH_4} \rightarrow \mathrm{CH_5^+} + \mathrm{CH_3} \\
&\mathrm{CH_5^+} + \mathrm{M} \rightarrow \mathrm{CH_4} + \mathrm{MH^+}
\end{aligned}$$

The protonated molecule formed ($[M + H]^+$, shown as MH^+ in the reaction scheme) provides information about the molecular weight of the compound, which can complement the information about structural composition obtained with EI [33].

While methane is the most common reagent gas, other gases can be used. The reagent gas can be chosen to target the specific proton affinity of an analyte of interest such that it is preferentially ionized. In addition to using CI to obtain protonated molecules, negative ions can be generated. Negative-mode chemical ionization can be a useful technique for many compounds with high electron affinity, including nitro-based organic explosives. Isobutane is the preferred reagent gas for negative CI of explosives, but methane can also be used [34, 35].

Electron ionization and CI are the ionization methods most readily coupled with GC, while **electrospray ionization** (ESI, not to be confused with EI) is the most common ion source to interface with LC. ESI is a straightforward way to generate gas-phase ions directly from a liquid at atmospheric pressure and without heating [36]. In ESI, a sample in solution is pumped through a needle that comes to a fine point with a small opening at the end. A high-voltage DC potential (4–6 kV) is applied to tip of the needle, while the inlet to the mass spectrometer is held at ground potential, resulting in an extreme electric field between the needle and the MS inlet. The high electric fields induce the liquid to spray toward the inlet in droplets with positive charges at the surface. As the droplets fly through the gap between the needle and the inlet, the solvent in the droplets dries rapidly and they shrink. The charges on the surfaces of the droplets are brought closer together and experience ever-increasing electrostatic repulsion. Eventually, the droplet shrinks to a point where the distance between charges is small and the repulsion is high enough that the droplet explodes in what is called a Coulomb explosion. Smaller droplets form out of the Coulomb explosion, which then also shrink and undergo their own Coulomb explosion. This process repeats until the sample has accumulated a positive charge and is no longer associated with a solvent droplet. In larger molecules (such as proteins and peptides), ions accumulate multiple charges during ESI. However, the small molecules that are the focus of forensic chemistry typically only form singly charged $[M + H]^+$ ions in positive-mode ESI. By switching the polarity of the source, negatively charged ions ($[M\text{-}H]^-$) can also be produced for negative-mode MS. Other adduct ions are also possible in ESI, particularly for explosives. It is not uncommon to observe $[M + NO_3]^-$ or $[M + Cl]^-$ ions in negative ESI for organic explosives containing nitro groups. In some cases, adding a small amount of a chloride salt to intentionally promote chloride adduct ($[M + Cl]^-$) formation can enhance sensitivity for explosives [37].

Atmospheric pressure chemical ionization (APCI) and ESI have a relationship similar to EI and CI. The engineering of APCI and ESI sources is closely related, even though the chemistry of ionization in the sources is quite different. Also, when an LC-MS system is purchased, it will likely come with an ESI source and the option to add an APCI source, which can be easily switched out with the ESI source. ESI is a very soft ion source, which is favorable for ionization of labile compounds like explosives, but it tends to perform poorly for more nonpolar compounds. The mechanism of APCI is more energetic, and many nonpolar compounds that do not ionize efficiently in ESI will do well when this source is exchanged for the APCI source [38]. Nearly, all instruments using an ESI or APCI ion source will be coupled to HPLC systems.

Similar to positive-mode CI, there is a cascade of reactions in an APCI source that results in the formation of reactive species that can transfer a proton to the analyte to form an $[M + H]^+$ ion. In the case of APCI, it is not necessary to add gas into the ion source because at atmospheric pressure, there is plenty of reactive gaseous N_2, O_2, and H_2O to function analogously to the reagent gas in CI. Electron beams are not sustainable at atmospheric pressure, so a glow discharge source is used instead. Instead of the high voltage being applied to a needle that has liquid flowing out of the tip, the high voltage is applied to a dry needle in open air. The high electric field at the tip generates an energetic plasma called a glow discharge which can be observed as a faint purple glow at the tip of the needle. The cascade of reactions that occurs in the reaction of the plasma with the atmospheric gases can be complex, but a common end point reactant is gaseous H_3O^+ and related protonated water clusters. The sample solution is pumped through a heated nitrogen gas flow such that the sample is thermally vaporized. The heated gas stream containing the sample is directed toward the ion cloud formed in the plasma at the tip of the needle. As the sample collides with the protonated water, proton transfer can take place, yielding $[M + H]^+$ ions. Other, more energetic, ion–molecule reactions are also possible in an APCI source such that a molecular ion or adduct may be observed as the major peak and there is more likely to be fragmentation in an APCI source than in an ESI source.

1.3.3 The Quadrupole Mass Analyzer

The most commonly used mass analyzer is the **quadrupole mass filter**. Although it can be conceptually difficult to understand, it is relatively simple and inexpensive to engineer in practice. The resolution is set to unit mass on most commercial instruments, so that all *m/z* values measured are rounded to the nearest integer value, which is considered low resolution. The most common mass spectrometer in forensic chemistry (generally for GC-MS) consists of an EI source coupled to a quadrupole mass analyzer. The mass analyzer does not need to be high resolution in this instrument because the identification is based on the fragmentation spectrum, not an exact mass produced by a high-performance mass analyzer.

The motion of ions in a quadrupole consists of complicated three-dimensional paths that are best visualized using computer simulation. Qualitative explanations can only be superficial, but will suffice for purposes of this section. The quadrupole consists of two pairs of electrically connected rods, spatially arranged at the corners of a square. The paired quadrupole rods are represented in the top of Fig. 1.8.

In this representation, the red rods would be connected such that one was biased with the positive DC voltage and the other red rod would be negative. The blue rods would be paired in the same way, with one positive and the other negative.

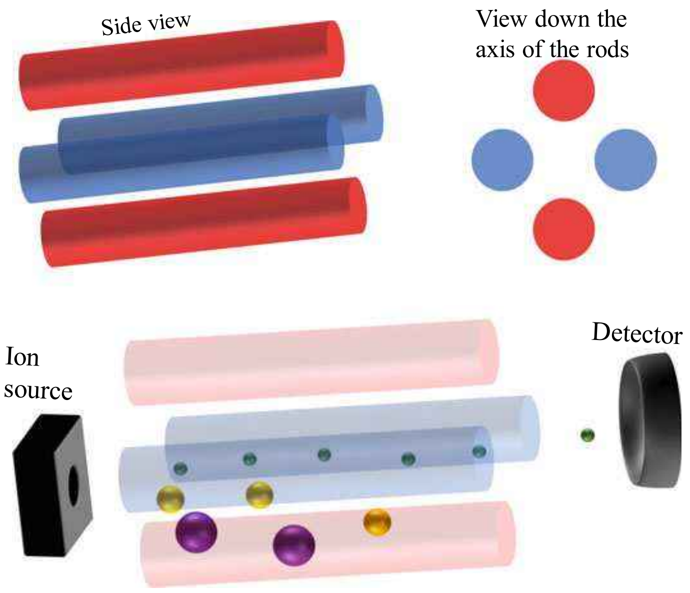


Fig. 1.8 Schematic of a quadrupole from two different views (top) and representation of a quadrupole functioning as a mass filter (bottom)

The arrangement of the rods creates a kind of tunnel, more easily seen in the view down the axis, which selected ions can travel through. In addition to DC voltage applied to the rod pairs, a radio frequency (rf) voltage is also applied to each pair. The red pair of rods and blue pair of rods would be 180 degrees out of phase. The electric field in the channel between the rods is complex and switching over time at the frequency of the rf voltage. Without a DC bias and at a low rf voltage, all ions have stable trajectories through the quadrupole. Filtering is achieved by altering the rf and DC values such that only a single ion can successfully pass through the analyzer at a time. This is illustrated at the bottom of Fig. 1.8. Three different *m/z* ions represented in green, yellow, and purple leave the ion source. The rf and DC values of the paired poles have been set such that only the *m/z* value of the green ion has a stable trajectory through the quadrupole and hits the detector to yield signal. The purple and gold ions are not stable at those rf and DC values; they are either ejected from the path through the center of the quadrupole or hit one of the rods and are neutralized. In either case, they do not reach the detector and would not contribute to the signal. After detection of the green ion, the rf and DC values would simultaneously increase in magnitude. At this new rf/DC setting, the green ion would no longer be stable and would not reach the detector. The next integer *m/z* value would now be stable, and any ions with that value would be detected. As the paired rf and DC values are increased in a synchronized manner, the value of the stable *m/z* is scanned over a set range. In this way, the quadrupole generates a spectrum by scanning the signal over a range of *m/z* values [39].

1.3.4 High-Resolution Mass Analyzers

Mass spectrometry is a potentially definitive technique, but the selectivity varies depending on the sample type, the specific ion source and mass analyzer being used, and whether the mass spectrometer is coupled with chromatography. Specific identification in mass spectrometry originates from either accurate mass measurements, fragmentation, or a combination of those. For a complete unknown, knowing that the mass is approximately 99 amu significantly narrows the field of possible compounds, but definitive identification cannot be made based only on that information. There are 100+ chemical formulas that correspond to a mass that rounds to 99 (e.g., C_3HO_3N, $C_4H_3O_3$, $C_3H_3O_2N_2$). The theoretical **accurate mass** of $^{35}Cl^{16}O_4$ is 98.9479627; perchlorate (with ^{35}Cl) is the only compound with that exact mass. Obtaining accurate mass measurements requires a high-resolution mass analyzer, which is more expensive. Additionally, definitive identification cannot be made based only on exact mass. Most organic compounds have isomers with the same chemical formula and therefore the same exact mass. For example, the high explosive RDX has a chemical formula of $C_3H_6N_6O_6$, corresponding to an exact mass of 222.0343334. Searching the CAS registry indicates that there are 32 other known compounds, besides RDX, with that same chemical formula, and therefore the same exact mass. An accurate mass measurement could narrow the possible compounds from the 140 million+ known compounds to 33. While not definitive, accurate mass spectra provide crucial information, particularly for compounds that were previously unknown or have not yet been entered into a spectral database. Most techniques (GC-MS, XRD, Raman, FTIR) are reliant on database searches and comparison with known standards. Even for compounds without an available known standard, accurate mass spectra can provide their elemental composition [40].

The most commonly encountered high-resolution mass analyzers in forensic chemistry laboratories are the time-of-flight (TOF) and Orbitrap mass analyzers [41, 42]. TOF is the less expensive mass analyzer (although still substantially more expensive than a quadrupole), but still has sufficient resolution to identify chemical formulas. Orbitrap mass analyzers have very high resolution and are easily capable of unambiguous determination of chemical formula for analytes. High-resolution mass analyzers are present in some forensic chemistry laboratories for analysis of drugs or explosives, but for ignitable liquids, high-resolution instruments generally are not necessary. Discussion of the specific mechanisms of these mass analyzers is beyond the scope of this text.

1.3.5 Tandem Mass Spectrometry

While the exact mass of a compound can provide a chemical formula, it is fragmentation that facilitates definitive identification with mass spectrometry. In GC-MS instruments with EI sources, the fragmentation occurs in the ion source.

Some mass spectrometers facilitate ion–molecule reactions that induce fragmentation in the mass analyzer. One advantage of this approach, which is known as tandem mass spectrometry or MS/MS, is that it is compatible with different types of ion sources. Further, a specific ion can be selected for fragmentation, whereas in EI all fragments are generated before mass selection in the analyzer. In most tandem mass spectrometry experiments, a mass analyzer is used to select a specific ion, which then enters a collision cell. The collision cell contains an inert gas (often He, N_2, or Ar) that collides elastically with the selected ion, causing it to fragment. This process is called collision-induced dissociation (CID). The fragments can then pass into a second mass analyzer that separates the fragments to yield an MS/MS spectrum. The most common tandem mass spectrometer is a **triple quadrupole** (QQQ) instrument, where the mass analyzer consists of an initial quadrupole mass filter, a second quadrupole that functions only as a collision cell for CID, and a third quadrupole that also functions as a mass filter [43, 44]. When coupled with LC as an LC-MS/MS system, these instruments are extremely sensitive and are useful for trace-level analysis of explosives [45]. Similar systems are also commercially available where a high-resolution mass analyzer is substituted for the third quadrupole. These instruments are expensive, but powerful, and are in use in some federal forensic chemistry laboratories. They combine the analytical power of both exact mass measurements and fragmentation spectra, allowing identification even for previously unknown compounds.

1.3.6 Chromatography Coupled to Mass Spectrometry

Most mass spectrometers used in forensic chemistry laboratories are not stand-alone instruments like FTIR or XRD instruments, but are coupled with a chromatographic system. Chromatography and mass spectrometry can be synergistic, with important disadvantages of each of the techniques overcome through this partnership. Chromatography does not have sufficient selectivity for identification, but definitive techniques such as mass spectrometry require that the sample be pure for identification. In a combined instrument, the chromatography can efficiently separate the components of the mixture prior to entering the mass spectrometer. Figure 1.9 illustrates this type of data. Figure 1.9 depicts the data produced by the GC-MS. The top of the figure shows the **total ion chromatogram (TIC)** which represents the total abundance of ions in the detector as a function of time. The bottom of the figure shows a mass spectrum of a specific time, indicated by the arrow.

While only one mass spectrum is shown, mass spectra are acquired throughout the chromatographic run, such that there are mass spectra for each of the peaks in the chromatogram. Note that if the compounds are not sufficiently separated from each other in the chromatography step, the quality of the mass spectra will be diminished. Even without baseline separation in the chromatogram, valuable information about complex mixtures can be obtained using GC-MS. Instead of

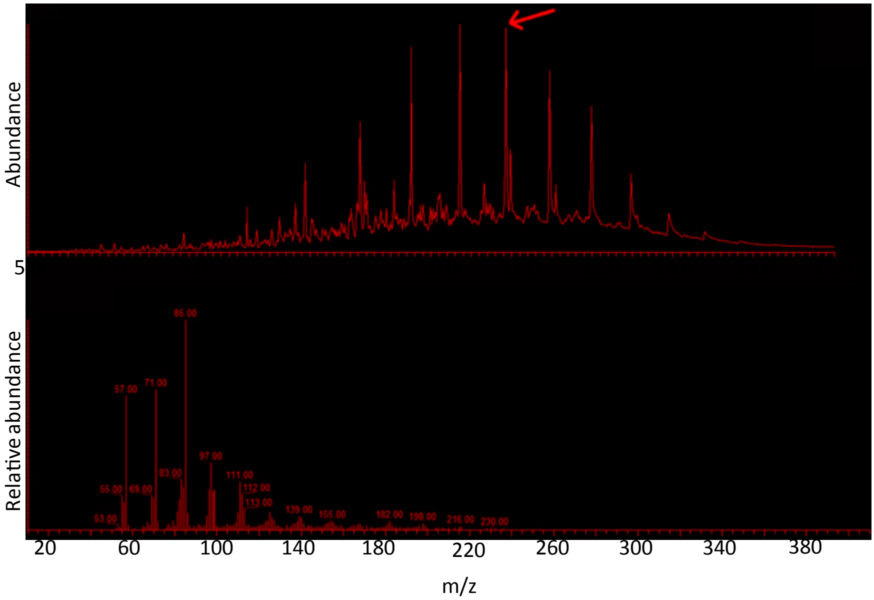


Fig. 1.9 Gas chromatography–mass spectrometry data for a sample of diesel fuel. Courtesy of Perry Michael Koussiafes, Bureau of Forensic Science, Havana, FL

viewing the TIC, the chromatographic data can be viewed as the abundance for a selected single ion or sum of the abundance group of ions. This technique is essential to the analysis of ignitable liquids and will be discussed further in Sect. 2.5.2.

While GC-MS instruments are the most commonly encountered mass spectrometers in forensic chemistry, LC-MS and IC-MS are increasingly being used in casework. The quality of the spectra improves significantly with the use of LC not only because there is retention time data to complement the mass spectra, but also because contaminants in the sample that could interfere with ESI or APCI are separated from the analyte during the chromatography. Ion chromatography also benefits from the use of a mass spectrometer as a detector. The identification of ions is definitive when the mass of the eluted ions is known in addition to the retention time.

1.4 Vibrational Spectroscopy Methods

1.4.1 Spectroscopy Background

Spectroscopy was briefly discussed in Sect. 1.2.2 in the context of HPLC detectors. **Absorbance** is a measurement of how much of the light impinging on a sample has

Table 1.2 Properties of electromagnetic radiation used in forensic analysis

Electromagnetic region	Wavelength (nm)	Wavenumber (cm^{-1})	Energy (eV)	Sample interaction
Mid-infrared	25,000–2500	400–4000	0.5–0.05	Bond excitation
Near-infrared	2500–700	3850–14,300	0.5–2	Bond excitation
Visible	700–400	>14,000	2–3	Electron excitation
Ultraviolet	400–190	N/A	3–7	Electron excitation
Vacuum ultraviolet	190–10	N/A	7–120	Electron excitation/ ejection
X-rays	0.01–10	N/A	120–120,000	Core electron ejection

been converted to excitation within a bond or atom. When the energy of a photon impinging on matter corresponds to a specific energy level present in the matter, the photon can be absorbed. The effect of this absorbance depends on the energy of the incoming photon, as shown in Table 1.2. The energy of the photon can be expressed as wavelengths or wavenumbers, which is simply the inverse of wavelength. In the case of UV light, photon energies primarily correlate with energy levels of electrons held in π bonding orbitals and heteroatoms. Excitation by UV light promotes an electron to a higher electronic state, which then relaxes back to the ground state and releases thermal energy. Electrons in π orbitals of conjugated double bonds are particularly effective UV absorbers, but nearly any compound with at least one double bond can be observed with a UV detector.

Unlike absorbance measurements in the UV region, which provide limited information about identity, information-rich infrared absorbance spectra can facilitate definitive identification. Each molecular bond has a specific energy (frequency) of vibration and rotation, and these energies generally correlate with IR energies. As such, infrared spectra provide specific information about molecular bonding.

1.4.2 Infrared Spectroscopy

Infrared spectroscopy has many advantages. It is nearly universal—almost all compounds, organic and inorganic, can absorb IR light. The small number of compounds that are not IR-active, such as NaCl, requires another technique for identification. For pure samples, it is a rapid and definitive technique that is much less expensive than other definitive techniques commonly used in forensic chemistry (i.e., mass spectrometry and X-ray diffraction) [46]. The major disadvantage of IR is that data interpretation for mixtures can be complicated. Extensive sample preparation, such as liquid–liquid or solid-phase extraction, is required to confidently identify individual components in a mixture using IR. Preliminary identifications of major components in mixtures can be accomplished using spectral deconvolution, which is typically built into the instrument software and can be used

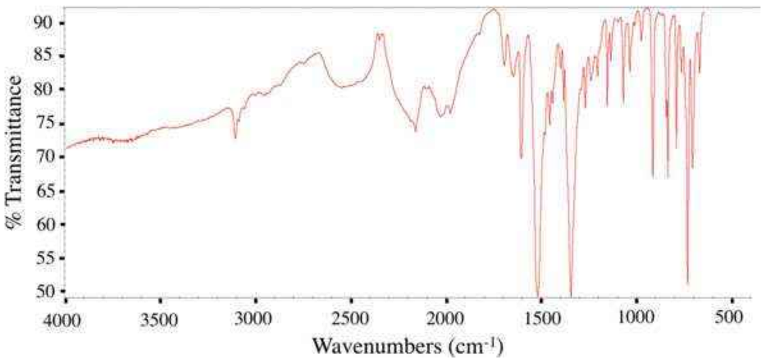


Fig. 1.10 Infrared spectrum of 2,4-dinitrotoluene. Data acquired by the author

for explosive mixtures [47]. However, minor components in mixtures are likely to be overlooked in IR analysis unless they are extracted and concentrated. Another practical disadvantage is that water has significant absorbance in the IR region and samples should be very dry for analysis to avoid interference from the water spectrum. Hygroscopic samples can be particularly problematic, especially in humid localities.

Spectra from the IR region can be plotted as absorbance versus wavelength as with UV data, but by convention they are typically plotted as percent transmittance vs wavenumber. A typical IR spectrum is shown in Fig. 1.10. The peaks in the spectrum correlate to specific bond energies being absorbed by the molecule, which gives an indication of the molecular structure and leads to identification of the molecule [48].

The instrumentation used to acquire IR spectra in forensic laboratories is the **Fourier transform infrared spectrometer (FTIR)**. In an FTIR instrument, the sample is exposed to all wavelengths of light from a broadband IR emitter simultaneously. As illustrated in Fig. 1.11, the light from the emitter is split by a beam splitter and reflected to the sample by two different mirrors. One of the mirrors has a fixed position, but the other is mounted on a stage that moves on a fixed path at a set rate. As it moves, the light from the moving mirror passes in and out of phase with the light from the fixed mirror. The light from the two mirrors experiences constructive and destructive interference as they interact. The detector measures the continuing decreasing and increasing intensity of the IR light as the position of the moving mirror changes. The signal intensity as a function of time (or mirror position) is an interferogram. The Fourier transform renders this signal into an intensity versus frequency plot, which is converted to transmittance versus wavenumber.

Because most compounds absorb in the IR, there is substantial background interference from atmospheric compounds. N_2 and O_2 are among the few

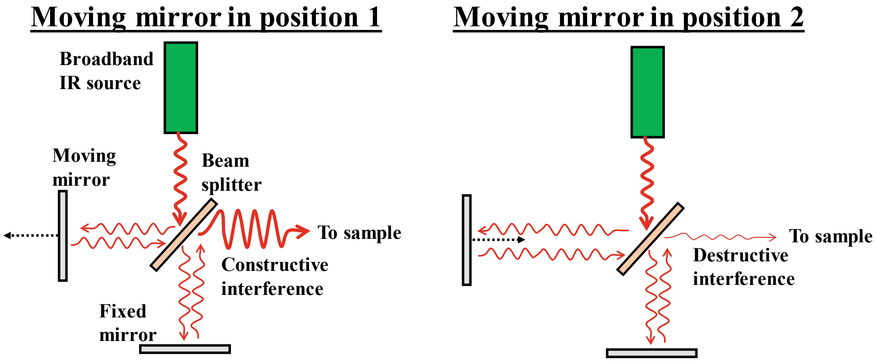


Fig. 1.11 Illustration on an interferometer in an FTIR instrument

compounds that do not absorb in the IR (and do not contribute to the background), but water vapor and carbon dioxide both absorb. The background is too daunting to be overcome through background subtraction alone. Fortunately, modern instruments overcome this limitation by acquiring multiple spectra and averaging them.

Samples should be analyzed as solids or neat liquids, rather than in solution as the solvent may absorb in the IR region. For traditional transmission IR, solid sample may be crushed to a fine powder along with a salt that does not absorb significantly in the IR, such as KBr. The sample/salt mixture can then be squeezed at high pressures in a pneumatic press to yield an IR transparent window, called a KBr pellet, that the beam can pass through. Most crime laboratories no longer use this approach as making KBr pellets can be difficult and time-consuming and requires a relatively large amount of sample. Oftentimes, a simpler, more convenient sampling technique called **attenuated total reflectance (ATR)** is used.

In an ATR sampling system, the sample is placed on top of a crystal made of a very high refractive index material such as diamond or germanium (Fig. 1.12). The sample is compressed against the crystal using a hand-tightened anvil. When light from the interferometer passes through the crystal and impinges on the sample, it is reflected. However, the light beam penetrates ~1 µm into the sample and absorbance based on the molecular bonds in the sample occurs. Several reflection events can occur within the crystal, depending on the instrument configuration, and absorbance occurs each time the beam interacts with the sample prior to reflection. The sample preparation is minimal compared to transmission IR, and substrates not amenable to crushing, such as plastic, can be easily analyzed. In theory, nanogram to microgram quantities can be measured [49]. In practice, milligram quantities of sample are often needed to obtain high signal-to-noise ratios without extensive sample preparation.

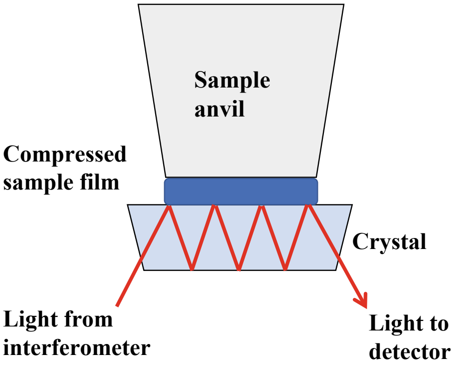


Fig. 1.12 Schematic of an ATR sampling accessory

1.4.3 Raman Spectroscopy

While both IR and **Raman spectroscopy** depend on molecular vibrations, IR is based on absorbance and Raman is based on scattering. Raman spectroscopy is a definitive technique and is complementary to FTIR. Instead of exposing the sample to a range of wavelengths, a sample for Raman analysis is exposed to a monochromatic source. Most of the light that encounters the sample will be transmitted, some will be absorbed, and a small portion of the light will be scattered by the sample. Most of the scattered light will have the same energy as the incident light; this is referred to as Rayleigh scattering. However, some of the scattered light undergoes Raman scattering, which is when the scattered photons have energies lower or higher than the impinging light. The light intensity from Raman scattering is a factor of 10^{-3} to 10^{-5} weaker than the intensity of the light from Rayleigh scattering [50, 51]. Raman scattering of lower and higher energy light is known as Stokes and anti-Stokes shifts, respectively. The spectrum of peaks for Stokes and anti-Stokes shifts is mirror images of each other, but the Stokes spectrum is higher intensity. Both types of scattering are unlikely events; very few of the photons impinging on the sample are actually scattered with a Stokes or anti-Stokes shift. This limits the sensitivity of the technique because the signal for the scattered light is a minor fraction of the intensity of the impinging light.

The use of lasers is a key to Raman; they provide a high-intensity, coherent, monochromatic light source that enhances the observed scattering signal [52]. Exposure to laser light can cause sample heating, which can be a concern with explosives [53]. An inexperienced examiner can experience unexpected excitement when analyzing black powder with a Raman instrument, as the sample can burn in dramatic fashion when the laser is turned on. In general, dark-colored samples should not be analyzed by Raman for safety reasons.

The most common Raman instruments are either dispersive instruments or Fourier transform. A dispersive Raman instrument will have a layout similar to the dispersive UV instrument shown in Fig. 1.4. After the laser beam impinges on the sample, a dispersion grating is used to separate the different wavenumbers of

Raman scattered light. The light is not collected from behind the sample, as it is in absorbance. Instead, backscattered light is emitted in all directions and background noise is reduced by collecting the light in front of or orthogonal to the sample. The spatially separated light is usually detected with a charge-coupled detector (CCD). A CCD functions similarly to the photodiode array, but has higher performance and is correspondingly more expensive. CCD detectors should be cooled for optimum performance, which can limit their use in portable instruments [54]. Fourier transform Raman (FT-Raman) instruments are similar in design to FTIR instruments. Most FT-Raman instruments used in forensic laboratories are actually dual FTIR instruments. For several commercial FTIR instruments, a Raman “add-on” attachment can be purchased. The instrument can then run FT-Raman using many components also used in FTIR analysis, including the interferometer, most of the optics, and detector. These instruments can switch between FTIR and FT-Raman with minimal effort. Because FTIR and Raman spectra yield complementary information, their data can be combined to increase certainty. For example, combined FTIR/Raman data has been effectively used for unequivocal identification of inorganic salts from low explosives. Some salts are more easily identified with FTIR, while others are more easily identified with Raman, such that the combined data enhances confidence in identification [55].

Raman has been used extensively in explosive analysis and provides several valuable contributions that supplement other techniques. Raman is nondestructive, unless the sample is degraded by the laser source, and can be noninvasive. Water is not Raman-active so aqueous samples that are challenging to analyze with other methods can be studied with Raman spectroscopy. Most plastics are transparent to Raman analysis, so samples can often be left in baggies or bottles and analyzed through the container walls if necessary. Raman is particularly useful for the detection of peroxide-based explosives, which can be difficult to detect with other methods [47].

Raman is also promising for standoff detection, where potential explosive devices can be analyzed at a distance for safe identification. Specialized Raman instruments have detected bulk explosive materials from a distance of 0.5 km [56]. Standoff identification is important for the safety of personnel investigating unexploded devices.

Both Raman and FTIR have been coupled with microscopes such that spectral data can be visualized spatially on samples. This has proved useful in explosives and trace evidence. As an example, small particles of explosive residue on a fingerprint can be located under the microscope and definitively identified using the Raman spectrum of the particle [57]. Explosive particles have also been located and identified on other types of evidence, including clothing and fingernails, using Raman microscopy [58].

The main limitation for Raman is low sensitivity due to the low occurrence of Stokes and anti-Stokes scattering as well as interference from fluorescence. Additionally, the molecule in question must be Raman-active to produce any useful signal, and many substances are not Raman-active. Finally, many of the portable Raman instruments have limited libraries for identification, so their use is generally limited to screening.

1.5 X-Ray Spectroscopy

1.5.1 Theory of X-Ray Spectroscopy

Unlike the vibrational spectroscopy techniques discussed earlier, which can provide molecular information, techniques using X-rays for excitation and/or detection are elemental techniques. The energy of X-rays is higher than UV or IR light and corresponds to the energy of core electrons within a particular atom (Table 1.2). X-ray photons or electrons from an accelerated electron beam are each energetic enough to displace electrons in core energy levels. When this happens, an electron from a higher energy level drops into the vacancy and the energy difference between its original state and the state it has fallen to is released as a photon. This photon has high energy, in the X-ray region, and the energy of the photons corresponds to the identity of the element [59].

To understand how X-ray excitation works, it will be helpful to briefly review atomic structure using a specific example. Consider magnesium, which has electrons in three fundamental quantum levels: $n = 1$, $n = 2$, and $n = 3$, in the electron configuration $1s^2 2s^2 2p^6 3\ s^2$. Analytical X-ray methods use the nomenclature K, L, and M to refer to electrons in the $n = 1$, $n = 2$, and $n = 3$ quantum states, respectively. In this nomenclature, magnesium has 2 K electrons, 8 L electrons, and 2 M electrons. If an energetic electron or X-ray photon causes the ejection of a K shell electron from the magnesium atom, an electron from a higher energy quantum level, an L or M electron, will fall into the state left empty by the ejected K electron and emit a photon carrying the energy difference between the two states [59].

Each element will have multiple characteristic X-ray energies corresponding to electron transitions between energy levels. Electrons can be ejected from the **K, L, or M shells**, and the electrons that replace the ejected electron can fall from multiple energy levels. With the example of magnesium, a vacancy generated by ejection of a K electron could be filled by an electron from either the L shell or the M shell. The X-ray photon released from the transition of an L electron to the K shell is termed a K_α X-ray, while the higher energy photon from the M to K shell transition is termed K_β. An electron ejected from the L shell would be replaced by an electron from the M shell, yielding the L_α X-ray. Magnesium is a small element for X-ray analysis, with only 12 electrons. For larger elements, which contain numerous electrons, the X-ray spectra get correspondingly more complex and information-rich.

Both X-ray fluorescence and energy-dispersive X-ray spectroscopy (EDS) yield X-ray spectra with lines corresponding to the elemental composition of the sample. However, XRF excites the core electrons using X-rays while EDS uses an energetic electron beam from a scanning electron microscope (SEM). One disadvantage of X-ray spectroscopy is that it is biased toward heavier elements. As the atomic mass of the analyte decreases, sensitivity decreases dramatically.

1.5.2 X-Ray Fluorescence

X-ray fluorescence (XRF) is a straightforward method for acquiring elemental information from samples. Because it is simple and nondestructive and requires little or no sample preparation, it has been used extensively in forensic science. While primarily used in trace evidence analysis for glass and paint chips [60], it is also useful for examining the elemental composition of explosives and components of explosive devices. Much of the information obtained from XRF can also be obtained using SEM-EDS, and laboratories under budgetary constraints will often have one of these instrument types, but not both. Both instruments provide the elemental composition for solid samples with minimal sample preparation. While XRF and EDS are much less sensitive than other atomic spectroscopy techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), their convenience makes them the preferred elemental analysis methods for most forensic laboratories.

The major components in an XRF instrument are the source and the detector. The source generates X-rays which excite the sample, resulting in the emitted characteristic X-rays. The most common source is a sealed X-ray tube which is under vacuum and contains a metal anode and a filament to produce electrons. The power applied to the X-ray source is a critical parameter in the sensitivity of the instrument and one of the main factors that differentiates commercial instruments [61]. The electrons are accelerated under high voltage and strike the metal anode, causing X-rays to be emitted. To produce a continuum of energies, which is needed to excite a broad range of elements in the sample, the electron beam is accelerated to energies beyond what is necessary for emission of K- and L-type X-rays. As this highly energetic electron beam approaches the anode, the electrons experience repulsion from the electron cloud in the metal anode and slow down, releasing a broad range of X-ray energies in the process. The X-rays' radiation resulting from this process is known as bremsstrahlung ("braking") radiation and is desirable in an X-ray source. However, this process can also occur as the X-rays from the source approach the sample, increasing the noise in the spectrum by adding background X-rays not characteristic of the sample [62].

As the X-rays formed exit the source, a slit is used to form a beam which then interacts with the sample. The result is the emission of characteristic X-rays as described in Sect. 1.5.1. Modern XRF instrumentation can be either configured such that the emitted X-rays are separated by wavelength, which correlates with energy, before being detected (wavelength-dispersive), or whether all energies of emitted X-rays impinge simultaneously on a detector capable of sorting their individual energies (energy-dispersive). Wavelength-dispersive instruments have higher resolution and improved performance for lower Z elements (capable of analysis down to oxygen), while energy-dispersive instruments are generally less expensive and simpler to operate and can be made portable [63]. Indeed, handheld "point and shoot" XRF instruments are widely commercially available and are the most straightforward method for determination of elemental sample composition in the field [64].

In wavelength-dispersive XRF (WDXRF) instruments, the emitted X-rays are directed to a crystal which causes diffraction of the light according to wavelength. The net effect is that the X-rays are physically dispersed according to their energies. The detector is placed behind a slit at an angle from the dispersing crystal such that only one wavelength of X-ray passes through. By precisely rotating the angle of the dispersing crystal, the specific wavelength of X-ray that passes through to the detector is changed; the entire range of wavelengths is scanned using careful rotation of the dispersing element.

In an energy-dispersive XRF (EDXRF) detector, all wavelengths of emitted X-rays impact a solid-state semiconductor-based detector simultaneously. The detector provides a measure of X-ray signal intensity (Y-axis in an X-ray spectrum) and determines their energies (X-axis) without the use of a separate dispersive element as is used in WDXRF. Interaction of X-rays with the body of a semiconductor detector creates free electrons, which are accelerated toward a collector plate using high voltage. The intensity of the signal caused by the electron impact with the collector plate is proportional to the energy of the X-ray that generated the electron [61].

1.5.3 Scanning Electron Microscopy–Energy-Dispersive Spectroscopy (SEM-EDS)

Many forensic laboratories already have scanning electron microscopes (SEMs), and relative to the cost of the SEM, energy-dispersive spectroscopy (EDS) is an inexpensive add-on. The SEM produces images of a sample by bombarding it with an electron beam and detecting the resulting backscattered electrons. As discussed in Sect. 1.6, impacting solid samples with energetic electrons can yield characteristic X-rays.

In SEM, an electron beam is generated by a filament and accelerated toward the sample using high voltage. When the electron beam impacts the sample, numerous interactions can occur. Mainly, backscattered electrons are reflected from and secondary electrons are emitted by the bombarded sample. A detector measures the intensity of the electrons from the sample as the electron beam is scanned across the surface. The intensity of backscattered electrons at each point is processed like the intensity of light measured by each pixel in a digital camera. The combined intensities at each of these “pixels” produce a full topographical image of the scanned sample area [65]. Very high magnifications, in excess of 40,000×, can be achieved in electron microscopy, and features on the order of hundreds of nanometers can be distinguished, though this level of resolution is rarely necessary in fire debris and explosive analysis [65].

Spectra in EDS are generated using solid-state energy-dispersive detectors, as is used in EDXRF. Note that the acronyms EDX and EDAX are synonymous with EDS. The electron gun used to generate the SEM images is also the source used to stimulate X-ray emission in the sample. SEM-EDS yields spatial elemental distribution, a capability that XRF does not provide. Specific spots in images can be chosen to acquire EDS spectra.

1.6 X-Ray Diffraction

X-ray diffraction (XRD) uses instrumentation similar to XRF and SEM-EDS to generate and measure X-rays; however, the analytical mechanism is fundamentally different. While the energy of emitted X-rays provides the qualitative information in XRF and SEM-EDS, identity information in XRD results from the angle of X-rays diffracted by the sample.

Information from X-rays diffracted by solid samples is used in several related analytical techniques, such as X-ray crystallography. However, in most of these techniques, the sample needs to be in a pure, well-formed crystal state; the sample has to be prepared by growing crystals. In fire debris and explosive analysis, the samples are generally small amounts of powdered solids. The type of XRD used for these samples is also known as powder diffraction. Minimal sample preparation is required for powder analysis, but samples are generally ground to a fine powder to improve the signal. XRD of powders requires relatively large amount of sample; at least milligram quantities are required. However, in many forensic samples, such as intact explosives, sufficient sample is available for XRD analysis. While XRD is relatively insensitive, it is highly selective. Compounds can be identified based on XRD data, known as diffractograms, with high confidence. The International Center for Diffraction Data maintains a database known as the Powder Diffraction File (PDF) which contains over 800,000 X-ray diffractograms [66, 67]. Commercial XRD instruments search the obtained diffractograms against the PDF. Additionally, XRD works well for organic and inorganic samples, provided that they have some crystalline structure. XRD is often used in concert with FTIR and SEM-EDS. Each of these techniques can analyze bulk powders, requires no significant sample preparation, and provides complementary information. These qualities make XRD an excellent technique for explosive analysis and for analysis of trace evidence in general [68, 69].

Similar to SEM-EDS and XRF, an XRD instrument consists primarily of an X-ray source, sample holder, and X-ray detector. The data is derived from incident angle of detection; therefore, the angles between the source, sample, and detector are carefully controlled. Because the information from XRD is not based on X-ray energy, the X-ray source for the analysis is monochromatic. A highly pure anode material, often copper, is used to emit characteristic X-rays, and a filter is used in the incident beamline to remove all but one wavelength.

X-rays impinging on the sample are diffracted depending on the molecular and crystalline structure of the sample. Diffracted X-rays experience constructive and destructive interference based on the angle of incidence and the atomic spacing within the structural order of the solid. At specific angles that correlate with the atomic spacing, the diffracted X-rays will experience nearly complete constructive interference. The intensity of the X-rays hitting the detector at this angle will be high, resulting in a peak. A range of angles, denoted as 2θ, is scanned by coordinating the rotation of the detector (Fig. 1.13) with the measured intensity, resulting in a plot of intensity versus 2θ. A typical diffractogram is shown in Fig. 1.14. The 2θ angle values that yield peaks correspond to the specific arrangement of atoms in that compound and can allow for definitive identification [63].

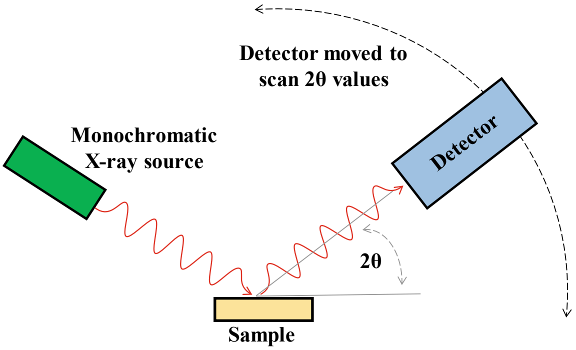


Fig. 1.13 Schematic of an X-ray diffraction analysis of a powder sample

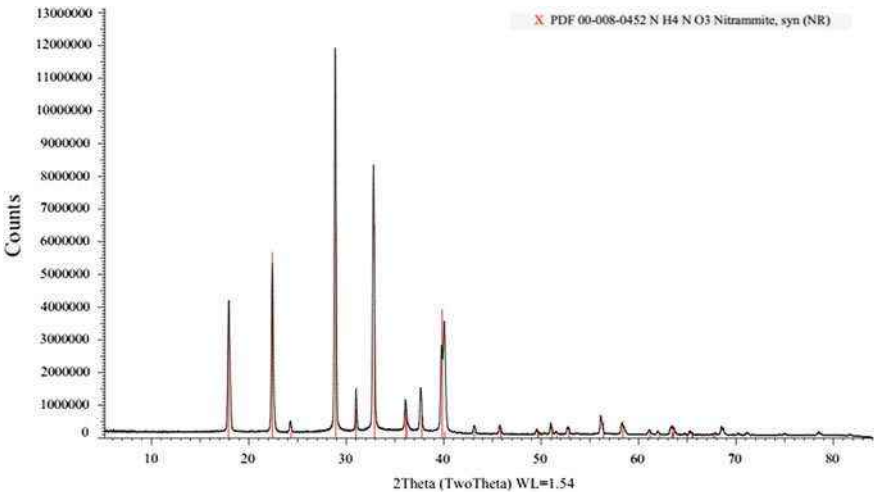


Fig. 1.14 X-ray diffraction pattern of ammonium nitrate. Courtesy of Michelle Evans, Bureau of Alcohol, Tobacco, Firearms, and Explosives. Note that this figure is identical to Fig. 10.1

XRD has the advantage that, like Raman spectroscopy, it is effective for analysis of both inorganic and organic components. Depending on how the sample is prepared, it is possible that certain lines, corresponding to particular crystal orientations, will be overrepresented in the sample. This phenomenon is known as preferred orientation. In preferred orientation, the crystals in the sample are preferentially oriented in one particular direction, artificially inflating the contribution of that particular phase. Preferred orientation can be avoided by careful sample preparation, such as thorough grinding of samples. Care must be taken in preparation for XRD samples to avoid preferred orientation. An example of preferred orientation and a mitigation technique will be discussed in Chap. 8. Unfortunately, XRD is not easily coupled to chromatography so the resulting diffractograms are often representative of mixtures. In the case of an impure sample, the confidence in identifying each single component in the mixture is somewhat reduced, but XRD is more selective for components of mixtures than FTIR.

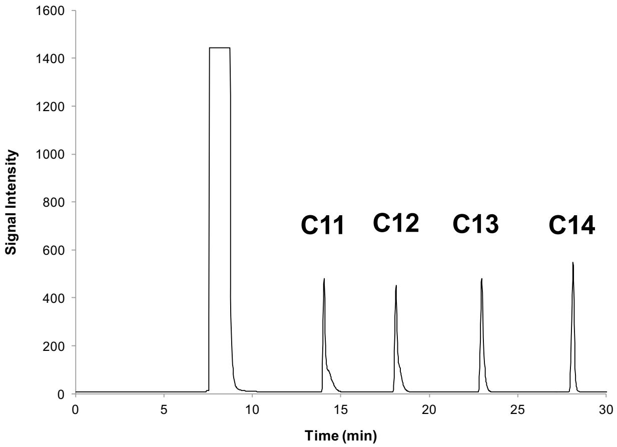
1.7 Summary

A broad variety of instrumentation is used in the analysis of fire debris and explosives, and an understanding of the strengths and weaknesses of each is essential. In the analysis of an unknown mixture, it is often useful to combine techniques to ensure that the components of the mixture are accounted for. For example, IR is an excellent definitive technique for pure samples, but it may miss lesser components of a mixture, or it may have difficulty with complex mixtures. Related compounds, such as various nitrate salts, can appear very similar in IR analysis; while they can be differentiated by their peak locations and the number of minor peaks, it is also useful to use an elemental technique like XRF or SEM-EDS to confirm the elements that are present. Similarly, XRD can be a definitive technique, but combining SEM-EDS data with XRD data gives an extra level of assurance that the compounds being identified make sense. By understanding the instruments in the laboratory's arsenal, the examiner can be flexible and creative with their analysis, which is necessary considering the broad variety of samples that may be encountered.

1.8 Questions

1. In forensic science, it is often necessary to explain complex instrumentation to non-scientists who may serve as jurors. Create analogies or simple explanations for GC, MS, and FTIR. After you have finished writing your explanations, find a volunteer who does not work in science and does not have a science degree. Read them your explanations and have them give you honest feedback about what they did and did not understand.

2. Neutron activation analysis (NAA) is a highly sensitive technique for elemental analysis. In NAA, a trained radiochemist places the sample into a nuclear reactor where it is bombarded with neutrons. The sample then emits high-energy light (gamma rays) that are detected and plotted in a spectrum. NAA is much more sensitive than XRF or SEM-EDS and gives more definitive elemental analysis. However, it is extremely rarely used in forensic chemistry and instrumentation for NAA is not found in any local or federal crime laboratories. Explain why.
3. Explain what split and splitless injection techniques are. Describe when you would want to use a split injection and when you might want to use a splitless injection.
4. The chromatogram shown below is from injection of a mixture of n-undecane (C11), n-dodecane (C12), n-tridecane (C13), and n-tetradecane (C14) in a pentane solvent.

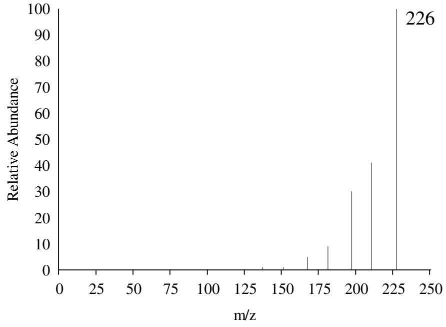


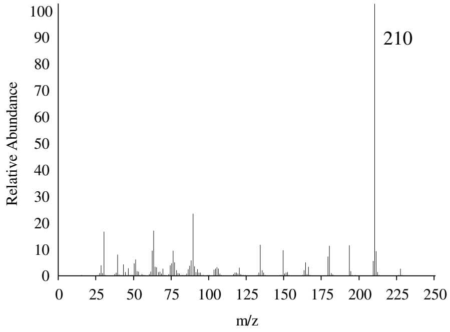
The column is a 100% methyl(DB-1) capillary column, and a temperature program was used: 70 °C held for 5 min and then a temperature increase of 10 °C/min until the end of the run at 30 min. Use this information to answer the following questions:

(a) What is the origin of the large peak at ~9 min?
(b) What was the temperature of the oven when n-dodecane eluted?
(c) What type of detector could have been used for this analysis? Would an ECD detector be appropriate? How about a quadrupole mass spectrometer with an EI ion source?

5. Suppose that you are obtaining a UV–Vis spectrum and FTIR spectrum of a sample. However, you have decided not to take a background spectrum before any of your sample spectra. Not getting a UV–Vis background spectrum will only slightly affect the quality of the UV–Vis spectrum for your sample. However, not getting an FTIR background before obtaining the FTIR spectrum of your sample will severely affect the quality of the FTIR spectrum for your sample. Briefly explain.

6. Draw a basic block diagram for a hybrid chromatography–mass spectrometer system and label all components. You will need to select a specific type of chromatography. For the mass spectrometer, select a specific ion source, mass analyzer, and detector. Describe what analytes this system would work well for and what it would not work well for.
7. The two mass spectra shown below [70, 71] are both for the organic explosive 2,4,6 trinitrotoluene ($C_7H_5N_3O_6$, MW = 227.1 g/mol) and were both acquired using a quadrupole mass analyzer. One of the spectra was obtained using an EI source, and one was obtained using negative-mode CI.





State which spectrum was acquired with which ionization source and justify your answer. Next identify the ion corresponding to the largest peak in each spectrum, using information about the common ions observed. Each is labeled with its *m/z* value.

References

1. Vessman J, Stefan RI, van Staden JF et al (2001) Selectivity in analytical chemistry (IUPAC Recommendations 2001). Pure Appl Chem 73:1381–1386. https://doi.org/10.1351/pac200173081381
2. Prichard E, Barwick V (2007) Quality assurance in analytical chemistry, 1st edn. Wiley-Interscience, Chichester, Hoboken, Teddington, Middlesex
3. CAS, Assigns the 100 millionth CAS registry number to a substance designed to treat acute myeloid leukemia. http://support.cas.org/news/media-releases/100-millionth-substance. Accessed 30 Mar 2018
4. CAS, Chemical abstracts service home page. http://support.cas.org/index. Accessed 30 Mar 2018
5. Webster GK, Diaz AR, Seibert DS et al (2005) Plate number requirements for establishing method suitability. J Chromatogr Sci 43:67–72. https://doi.org/10.1093/chromsci/43.2.67
6. Jorgenson JW (2010) Capillary liquid chromatography at ultrahigh pressures. Annu Rev Anal Chem 3:129–150. https://doi.org/10.1146/annurev.anchem.1.031207.113014
7. Lindsay S (1992) High performance liquid chromatography, 2nd edn. Wiley, Chichester, New York
8. Harris DC (2006) Quantitative chemical analysis, 7th edn. W. H. Freeman, New York
9. McNair HM, Miller JM (1997) Basic gas chromatography, 1st edn. Wiley-Interscience, New York
10. McCord B, Corbin I, Bender E (2011) Chromatography of explosives. In: Forensic investigation of explosions, 2nd edn. CRC Press, Boca Raton, p 36
11. Fowlis IA (1995) Gas chromatography: Analytical chemistry by open learning, 2nd edn. Wiley, Chichester, New York
12. Douse JMF (1981) Trace analysis of explosives at the low picogram level by silica capillary column gas—liquid chromatography with electron-capture detection. J Chromatogr A 208:83–88. https://doi.org/10.1016/S0021-9673(00)87965-0
13. Gregory KE, Kunz RR, Hardy DE et al (2011) Quantitative comparison of trace organonitrate explosives detection by GC-MS and GC-ECD2 methods with emphasis on sensitivity. J Chromatogr Sci 49:1–7. https://doi.org/10.1093/chrsci/49.1.1
14. Hetrick EM, Schoenfisch MH (2009) Analytical chemistry of nitric oxide. Annu Rev Anal Chem 2:409–433. https://doi.org/10.1146/annurev-anchem-060908-155146
15. Jimenez A (2004) Chemiluminescence detection systems for the analysis of explosives. J Hazard Mater 106:1–8. https://doi.org/10.1016/j.jhazmat.2003.07.005
16. Dicinoski GW, Shellie RA, Haddad PR (2006) Forensic identification of inorganic explosives by ion chromatography. Anal Lett 39:639–657. https://doi.org/10.1080/00032710600609735
17. Abramovich-Bar S, Bamberger Y, Ravreby M, Levy S (1993) Applications of ion chromatography for determination and identification of chlorate, nitrite and nitrate in explosives and explosive residues. Advances in analysis and detection of explosives. Springer, Dordrecht, pp 41–54
18. Barron L, Gilchrist E (2014) Ion chromatography-mass spectrometry: a review of recent technologies and applications in forensic and environmental explosives analysis. Anal Chim Acta 806:27–54. https://doi.org/10.1016/j.aca.2013.10.047
19. Lang GL, Boyle KM (2009) The analysis of black powder substitutes containing ascorbic acid by ion chromatography/mass spectrometry. J Forensic Sci 54:1315–1322. https://doi.org/10.1111/j.1556-4029.2009.01144.x
20. Majors R (2013) Ion chromatography: yesterday, today, and tomorrow. LC GC 31:7
21. Nesterenko PN, Paull B (2017) Ion chromatography. In: Liquid chromatography. Elsevier, Amsterdam, pp 205–244

22. Light TS, Licht SL (1987) Conductivity and resistivity of water from the melting to critical point. Anal Chem 59:2327–2330. https://doi.org/10.1021/ac00146a003
23. Dasgupta PK, Shelor CP, Liao H (2013) Ion chromatography yesterday and today. LC GC 31:23–26
24. Macdonald JC (1985) Inorganic chromatographic analysis. Wiley, New York
25. Stevens TS, Davis JC, Small H (1981) Hollow fiber ion-exchange suppressor for ion chromatography. Anal Chem 53:1488–1492. https://doi.org/10.1021/ac00232a044
26. Small H, Stevens TS, Bauman WC (1975) Novel ion exchange chromatographic method using conductimetric detection. Anal Chem 47:1801–1809. https://doi.org/10.1021/ac60361a017
27. Whatley H (2001) Basic principles and modes of capillary electrophoresis. Clinical and forensic applications of capillary electrophoresis. Humana Press, Totowa, pp 21–58
28. McLafferty FW, Tureek F (1993) Interpretation of mass spectra, 4th edn. Univ Science Books, Mill Valley, Calif
29. Harrison AG, Cotter RJ (1990) Methods of ionization. In: Methods in enzymology. Academic Press, Cambridge, pp 3–37
30. Munson B (1971) Chemical ionization mass spectrometry. Anal Chem 43:28A–43A
31. Munson MSB, Field FH (1966) Chemical ionization mass spectrometry. I. general introduction. J Am Chem Soc 88:2621–2630. https://doi.org/10.1021/ja00964a001
32. Koenig JL (1999) Chapter 10—Mass spectrometry of polymers. In: Koenig JL (ed) Spectroscopy of polymers, 2nd edn. Elsevier Science, New York, pp 441–480
33. Herbert CG, Johnstone RAW (2002) Mass spectrometry basics, 1st edn. CRC Press, Boca Raton
34. Dougherty RC (1981) Negative chemical ionization mass spectrometry. Anal Chem 53:625A–634A
35. Yinon J (1980) Analysis of explosives by negative ion chemical ionization mass spectrometry. J Forensic Sci 25:12145J. https://doi.org/10.1520/JFS12145J
36. Whitehouse CM, Dreyer RN, Yamashita M, Fenn JB (1985) Electrospray interface for liquid chromatographs and mass spectrometers. Anal Chem 57:675–679. https://doi.org/10.1021/ac00280a023
37. Yinon J (2003) Analysis of explosives by LC/MS. In: Advances in forensic applications of mass spectrometry. CRC Press, Boca Raton
38. Gross JH (2017) Mass spectrometry: a textbook, 3rd edn. Springer, New York
39. Miller PE, Denton MB (1986) The quadrupole mass filter: basic operating concepts. J Chem Educ 63:617
40. Biemann K (1990) Utility of exact mass measurements. In: Methods in enzymology, vol 193. Academic Press, Cambridge, pp 295–305
41. Cotter RJ (1997) Time-of-flight mass spectrometry: instrumentation and applications in biological research, 1st edn. American Chemical Society, Washington, DC
42. Hu Q, Noll RJ, Li H et al (2005) The orbitrap: a new mass spectrometer. J Mass Spectrom 40:430–443. https://doi.org/10.1002/jms.856
43. Yost RA, Boyd RK (1990) Tandem mass spectrometry: quadrupole and hybrid instruments. In: Methods in enzymology, vol 193. Academic Press, Cambridge, pp 154–200
44. Yost RA, Enke CG (1979) Triple quadrupole mass spectrometry for direct mixture analysis and structure elucidation. Anal Chem 51:1251–1264. https://doi.org/10.1021/ac50048a002
45. Yinon J, McClellan JE, Yost RA. Electrospray ionization tandem mass spectrometry collision-induced dissociation study of explosives in an ion trap mass spectrometer. Rapid Commun Mass Spectrom 11:1961–1970. https://doi.org/10.1002/(SICI)1097-0231(199712)11:18%3c1961::AID-RCM99%3e3.0.CO;2-K
46. Smith B (2011) Introduction to infrared spectroscopy. In: Fundamentals of fourier transform infrared spectroscopy, 2nd edn. p 18

47. Zitrin S, Tamiri T, Tamiri S (2011) Analysis of explosives by infrared spectrometry. In: Forensic investigation of explosions, 2nd edn. CRC Press, Boca Raton, pp 671–690
48. Skoog DA, Holler FJ, Crouch SR (2006) Principles of instrumental analysis, 6th edn. Brooks Cole, Belmont
49. Brown K, Greenfield M, McGrane S, Moore D (2016) Advances in explosives analysis-part II: photon and neutron methods. Anal Bioanal Chem 408:49–65. https://doi.org/10.1007/s00216-015-9043-1
50. Woodward LA (1967) General introduction. Raman spectroscopy: theory and practice. Springer, US, pp 1–43
51. Nakamoto K (2009) Infrared and raman spectra of inorganic and coordination compounds, part A: theory and applications in inorganic chemistry, 6th edn. Wiley-Interscience, Hoboken
52. Kuligowski J, Lendl B, Quintás G (2017) Advanced IR and Raman detectors for identification and quantification. In: Liquid chromatography. Elsevier, Amsterdam, pp 463–477
53. Moore DS (2004) Instrumentation for trace detection of high explosives. Rev Sci Instrum 75:2499–2512. https://doi.org/10.1063/1.1771493
54. Smith E, Dent G (2005) Modern Raman spectroscopy: a practical approach. Wiley, Hoboken, p c2005
55. Zapata F, García-Ruiz C (2018) The discrimination of 72 nitrate, chlorate and perchlorate salts using IR and Raman spectroscopy. Spectrochim Acta A Mol Biomol Spectrosc 189:535–542. https://doi.org/10.1016/j.saa.2017.08.058
56. Wallin S, Pettersson A, Östmark H, Hobro A (2009) Laser-based standoff detection of explosives: a critical review. Anal Bioanal Chem 395:259–274. https://doi.org/10.1007/s00216-009-2844-3
57. Emmons ED, Tripathi A, Guicheteau JA et al (2009) Raman chemical imaging of explosive-contaminated fingerprints. Appl Spectrosc 63:1197–1203. https://doi.org/10.1366/000370209789806812
58. Hargreaves MD (2012) Drugs of abuse—application of handheld FT-IR and Raman spectrometers. In: Chalmers JM, Edwards HGM, Hargreaves MD (eds) Infrared and Raman spectroscopy in forensic science. Wiley, New York, pp 339–349
59. Lawes G (1987) Scanning electron microscopy and X-Ray microanalysis, 1st edn. Wiley, Chichester, New York
60. Bisbing RE (2006) Trace evidence in the real crime laboratory. In: Mozayani A, Noziglia C (eds) The forensic laboratory handbook. Humana Press, Totowa, pp 265–290
61. Sherma J, Larkin JD, Larkin FH (2007) X-Ray fluorescence spectrometry. J AOAC Int 90:163A–170A
62. Shackley MS (2011) An introduction to X-Ray fluorescence (XRF) analysis in archaeology. In: Shackley MS (ed) X-Ray fluorescence spectrometry (XRF) in geoarchaeology. Springer, New York, pp 7–44
63. Jenkins R (1999) X-Ray fluorescence spectrometry, 2nd edn. Wiley, New York
64. Cesareo R, Gigante GE, Castellano A, Ridolfi S (2009) Portable and handheld systems for energy-dispersive X-ray fluorescence analysis. In: Meyers RA (ed) Encyclopedia of analytical chemistry. Wiley, Chichester
65. Reimer L (1998) Scanning electron microscopy: physics of image formation and microanalysis, 2nd edn. Springer, Berlin, Heidelberg
66. Smith DK, Jenkins R (1996) The powder diffraction file: past, present, and future. J Res Natl Inst Stand Technol 101:259–271. https://doi.org/10.6028/jres.101.027
67. ICDD—International Centre for Diffraction Data. http://www.icdd.com/. Accessed 18 Aug 2018
68. Kugler W (2003) X-ray diffraction analysis in the forensic science: the last resort in many criminal cases. Adv X-Ray Anal 46:1–16

69. Rendle DF (2003) X-ray diffraction in forensic science. Rigaku J 19:11–22
70. Stein SE. Mass spectra. In: NIST chemistry webbook, NIST standard reference database
71. Holmgren E, Ek S, Colmsjö A (2012) Extraction of explosives from soil followed by gas chromatography–mass spectrometry analysis with negative chemical ionization. J Chromatogr A 1222:109–115. https://doi.org/10.1016/j.chroma.2011.12.014

Kenyon Evans-Nguyen is Associate Professor and Director of the Forensic Science Program at The University of Tampa. He publishes in forensic chemistry, specifically in the development of new technologies and methods in forensic mass spectrometry.

Chapter 2
Introduction to Fire Debris Analysis

Jamie Baerncopf and Sherrie Thomas

Learning Objectives

- Become familiar with the role of fire debris analysis in the context of a fire investigation.
- Learn techniques for analyzing evidence for ignitable liquids.
- Understand the classification of ignitable liquids and data interpretation.
- Understand analyses outside of ignitable liquid analysis that may fall under the fire debris discipline.
- Learn appropriate report wording for fire debris results.

Fire is a pervasive problem that causes loss of money, property, and lives. Based on an estimate by the National Fire Protection Association (NFPA), over 1.3 million fires in the USA were responded to by a fire department in 2015. Intentional fires were the fourth leading cause of home structure fires [1]. The focus of fire debris analysis is to examine evidence related to fire investigations to identify the presence of ignitable liquids, information that may help investigators determine the origin and cause of the fire.

In a survey of fire debris cases in Canada, approximately 63% of the cases had at least one sample that contained an ignitable liquid and approximately 48% of submitted samples were positive, with 78% of those samples identified as containing gasoline [2]. Though these numbers are for a single country, they underscore the importance of fire debris analysis as an investigative tool.

J. Baerncopf (✉)
Bureau of Alcohol, Tobacco, Firearms and Explosives- Forensic Science Laboratory,
Walnut Creek, CA, USA

S. Thomas
Bureau of Alcohol, Tobacco, Firearms and Explosives- Forensic Science Laboratory,
Atlanta, CA, USA

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_2

2.1 From Scene to Laboratory

There is a great deal that happens in a **fire investigation** prior to submission of evidence to the laboratory. It is advantageous for an examiner to have a basic knowledge of what happens at the fire scene to better understand their role in the larger fire investigation. In a fire investigation, investigators seek to determine the **cause and origin** of a fire [3, 4]. The cause of the fire may be classified as accidental, natural, incendiary, or undetermined. Fire investigators use a systematic approach to investigate the fire and use their training and experience to evaluate fire patterns, potential ignition sources, fuel loads, fire progression, and other factors to determine what may have happened. As the fire investigator evaluates the fire scene, they may collect evidence to support their hypothesis of how and where the fire started. This is where the fire debris examiner fits in: typically, examiners analyze evidence recovered from or related to fire scenes to determine if any ignitable liquids are present. Common fire debris evidence includes debris from the scene, suspect or victim clothing, and liquids found at the scene or during the execution of a search warrant. Though closely linked to fire investigation, a fire debris examiner should avoid terms that are commonly used during investigations such as "arson" and "accelerant," both of which imply intent. The fire debris examiner should be unbiased and report the objective results of their analyses.

In addition to an investigator's training, tools may be used to help with sample selection at a fire scene. Accelerant detection canines and hydrocarbon detectors may be used by some investigators to help locate possible ignitable liquids. Though both canines and hydrocarbon detectors can offer excellent sensitivity, they generally lack the selectivity offered by gas chromatography–mass spectrometry (GC-MS) in the laboratory, due to the abundance of interferences at a fire scene. It is important to stress that canines, hydrocarbon detectors, and any on-scene detection methods are considered presumptive tests for ignitable liquids. Any on-scene alerts must be confirmed by laboratory analysis [3, 5].

Investigators may also collect **comparison samples**. Petroleum products are used in the manufacture of a wide variety of household materials [6]. Comparison samples may help determine if a matrix being examined, such as flooring or carpet, inherently contains an ignitable liquid. Comparison samples may also corroborate information from a home or business owner, such as the use of an insecticide on the baseboards of a residence or floor treatment in an office. The comparison sample should be the same as the material of interest and collected from an area believed to be free of any ignitable liquids. In cases in which a fire scene is overwhelmed with ignitable liquids or when a scene has been nearly completely consumed by the fire, collection of comparison samples may not be possible.

Because ignitable liquids easily evaporate, any items of evidence to be analyzed must be packaged in vapor-tight packaging to prevent sample loss and also to prevent contamination [7, 8]. The most common types of packaging for fire scene evidence are metal paint cans and bags specifically marketed for fire debris, as shown in Fig. 2.1. It is important to realize that common plastic storage bags are not

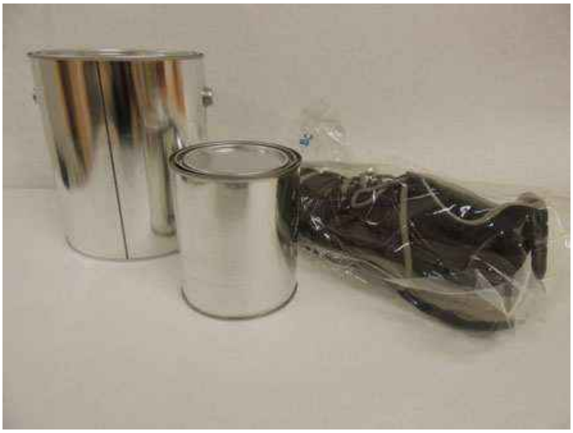


Fig. 2.1 Examples of proper fire debris packaging

vapor-tight and could allow for contamination or loss of sample. Other types of containers such as glass mason jars and vials are also acceptable. It is important to note that each of these types of packaging has its advantages and disadvantages which should be considered by the investigator collecting the evidence. Evidence submitted in boxes, paper bags, or other packaging that is not vapor-tight should not be analyzed for ignitable liquids as the evidence may have been exposed to outside contamination or any traces of ignitable liquid in the evidence may have been lost. It is also important that the evidence is packaged correctly at the time of collection as contamination can happen within as little as one hour [9].

2.2 Beginning a Fire Debris Case

A fire debris case begins as soon as the examiner has evidence in their custody. Generally, evidence is received at the laboratory through an evidence room [10]. The first step an examiner should take after receiving the evidence is to properly label the evidence containers and conduct an opening inventory [11]. The purpose of this inventory is to ensure that the examiner has all items of evidence that the investigator intended to submit. Any missing items need to be reconciled with the evidence room and/or evidence submitter.

After all evidence is accounted for, a quick visual examination should follow, again, to ensure that all items received are as described by the submitter. If an examiner has an item labeled suspect's clothing, but the item contains fire debris, then this discrepancy needs to be resolved. A quick visual examination may also help the examiner determine the best analysis scheme for each item of evidence, if materials from evidence collection are packaged with the exhibit that should be removed, such as gloves, swabs, or additional layers of packaging, or if further examinations such as fingerprints or DNA should be added.

Oftentimes, general investigative background information is submitted with the evidence, which may influence the analysis scheme of the examiner. For example, if the evidence is from a kitchen fire, vegetable oil analysis may be of interest to the investigator. Since screening for vegetable oils differs from typical ignitable liquid screening (see Chap. 4), an investigator may not know to request this type of analysis [12]. As such, the background information provided may aid in determining the most suitable analysis of the evidence. However, recent discussions within the forensic science community have expressed concern that knowing investigative information may bias the examiner [13, 14]. Individual laboratories may decide how to handle this potential issue in their own way.

2.3 Analysis of Fire Debris Evidence

The goal of fire debris analysis is to identify the presence of ignitable liquids in an item of evidence. An **ignitable liquid** is any liquid that will react with oxygen and produce a flame when subjected to an ignition source. Ignitable liquids include both flammable and combustible liquids, a distinction that is based on flash point. **Flashpoint** is the temperature at which a sample will create a flash flame when an ignition source is introduced. Flammable liquids have a flash point below 100 °F, and combustible liquids have a flash point at or above 100 °F [3]. Fire debris evidence can come in a variety of forms such as liquids and, more commonly, burned or unburned matrices including carpet and padding, wood, clothing (victim or suspect), shoes, or any material that may retain an ignitable liquid. Preparation of liquids for analysis is typically a simple dilution or may involve a liquid–liquid extraction if the liquid is aqueous, or water-based. Ignitable liquids that remain in the matrix are referred to as ignitable liquid residues (ILRs) and must be isolated by extraction. Several different extraction techniques have been utilized in fire debris analysis. The main types of extractions are distillation, solvent extraction, headspace, and adsorption-elution techniques [7, 15]. Each of these techniques has advantages and disadvantages. An understanding of each is important in determining the best analytical scheme for an item of evidence.

2.3.1 Liquids

Liquids are among the simplest samples to prepare in fire debris cases. These liquids may have been removed from a container, such as a red plastic gasoline can, or collected from a puddle with a sheen on the surface. An examiner should observe the properties of the liquid such as odor, color, and viscosity, and perform an **ignition susceptibility test (IST)**. An IST, in which a sample of the liquid is exposed to an open flame, is used to determine if the liquid is ignitable. Though the IST is a presumptive test, the ease of ignition, color of the flame, and presence/color of the smoke should be noted as it may give an examiner an idea of the type of liquid present. Gasoline and many other types of liquids typically burn with an orange flame and produce a dark-colored smoke. Conversely, oxygenated compounds, such as acetone or ethanol, tend to burn with a faint blue flame and produce little or no smoke.

If the liquid is ignitable, it may be diluted in an appropriate solvent such as carbon disulfide, pentane, or dichloromethane, and injected into the gas chromatograph–mass spectrometer. If the liquid is not ignitable, it may indicate that the liquid is aqueous. A quick test of pH may also be useful and can help protect the instrument from a strong acid or base being injected. Aqueous liquids can be extracted using an organic solvent such as carbon disulfide or pentane to separate any potential petroleum products. Further preparation of the liquid such as filtration or concentration of the extract may be required prior to analysis by GC-MS.

2.3.2 Extraction Techniques: Distillation

Distillation is one of the oldest extraction techniques used in fire debris analysis. This technique is mentioned here only for historical value as it has been long superseded by headspace techniques [7]. In steam distillation, water is added to the evidence and brought to a boil. As the water boils, vapors are produced and condensed into a separate container. In vacuum distillation, no water or solvents are used and the evidence is put under a vacuum to allow for the evaporation of volatile components. As with steam distillation, the volatilized components are condensed in a cooled trap. The resultant distillate could be then analyzed. Though these techniques were useful at the time, their elaborate setup, destructive nature, and comparative insensitivity have rendered them obsolete.

2.3.3 Extraction Techniques: Static Headspace

Static headspace is a technique in which a sample of the headspace above the evidence is removed by syringe and analyzed [16]. Some laboratories use static headspace as a screening technique because it is simple and nondestructive and requires only a short extraction time. It may be suitable for the extraction of low boiling compounds such as oxygenates and light petroleum products. However, disadvantages of this technique include poor recovery of heavier compounds and low sensitivity. In static headspace, the container is heated in an oven or heating mantle to a temperature between 60 and 90 °C. Heating allows for a greater concentration of volatile components in the sample to be converted to the headspace. However, the container should not be heated above 100 °C as that could cause dangerous overpressure problems with wet samples. Heating times can vary, but should be sufficient to allow for the sample to come to thermal equilibrium.

Using an airtight syringe, a sample of vapor is withdrawn from the headspace of the container and then injected into the GC injection port. The syringe should also be heated to avoid condensation of volatile components inside the syringe. An air blank using the same airtight syringe should be run before all samples to ensure that the syringe itself is clean.

2.3.4 Extraction Techniques: Adsorption

Adsorption techniques are, by far, the most commonly used techniques to extract ignitable liquid residues from a sample matrix. In adsorption techniques, volatile components in a sample are collected on an adsorbent and then removed via desorption for instrumental analysis [17–19]. Because the volatile components in the headspace accumulate on the adsorbent, they are effectively concentrated.

There are several parameters that must be considered with adsorption techniques. The first parameter to consider is the choice of adsorbent type. The most common adsorbent is activated charcoal due to the affinity of activated charcoal for the components found in ignitable liquids. Activated charcoal may be in granular form or is often used in the form of a polymer strip, which is a homogeneous mixture of activated charcoal and embedded Teflon. Other adsorbents include Tenax® and polymer-coated fibers used for solid-phase microextraction (SPME). After adsorption, desorption is required for analysis by GC-MS. Solvent desorption, also known as elution, is used in most techniques, though thermal desorption is used with SPME or Tenax®. There are a variety of solvents that can be used to desorb ignitable liquid components including pentane, dichloromethane, and diethyl ether; however, carbon disulfide has been shown to be best because it has a high affinity for activated carbon and effectively displaces the adsorbed components [7].

Another important factor is that adsorption techniques may be passive or dynamic/active. In passive methods, volatile compounds are allowed to diffuse onto the active sites of the adsorbent by placing the adsorbent in the sample headspace. Conversely, the headspace of the sample is pushed with a gas (positive) or drawn by vacuum (negative) through the adsorbent in dynamic mode (Fig. 2.2). Other parameters affecting recovery include temperature and time of exposure.

Passive Headspace Concentration

In passive adsorption, also referred to as **passive headspace concentration**, activated charcoal is placed in the headspace of the sample for a set amount of time (times generally range from 2 to 24 h) and at a set temperature (ambient or heated to 60–90 °C) (Fig. 2.2) [17]. Heating the sample drives the volatiles into the gas phase, allowing adsorption onto the activated charcoal. The sample container is then removed from the oven and cooled for safe handling. Once the adsorbent is removed from the container, it is eluted with a suitable solvent for analysis by GC-MS.

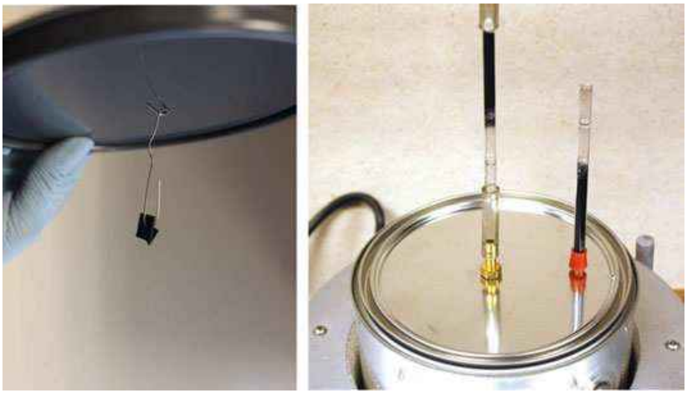


Fig. 2.2 Passive (left) and dynamic (right) headspace concentration setup. In passive headspace, the charcoal strip can be hung on a paper clip and attached to the underside of the can lid using a magnet on the outside of the can. In dynamic headspace, two packed charcoal tubes are inserted in the lid of the can for extraction

Historically, packed charcoal tubes have been used for passive headspace methods; however, they have been largely replaced by activated charcoal strips. Charcoal strips require little sample preparation, and an additional strip may be placed in the headspace during extraction to be retained with the evidence in case future analysis is required [20].

Passive headspace concentration is widely popular for several reasons. It is a very sensitive technique that is generally not destructive, so the sample may be re-extracted using another extraction technique, using different extraction parameters, or by another examiner. Though the samples can be prepared in batches unlike other techniques, the extraction time is typically long (8- to 24-h extractions are common).

There are extraction effects that should be considered when using passive headspace concentration. In this technique, volatile components are trying to achieve equilibrium on the adsorbent. Since adsorption is a weak physical attraction, components may be displaced by other molecules having a greater affinity for the adsorbent during the extraction period. With **displacement**, larger molecules are less likely to be dislodged from the adsorbent than smaller molecules, which leads to a possible overrepresentation of heavier components and skewing of data. Additionally, aromatic hydrocarbons preferentially adsorb to the activated charcoal over alkane components. This skewing is most often seen with very concentrated samples due to insufficient adsorption sites. In these instances, the data will reflect a shift toward the heavy end of the chromatogram or apparent artificially high aromatic content in the sample. These effects may also be seen with excessively long extraction times. Conversely, if extraction temperatures are too low or times are too short, the resultant data may underrepresent the heavy content in the sample due to insufficient volatilization of the heavier components. These issues should always be considered when deciding appropriate extraction parameters. If the data suggests that one of these issues may be a factor, an additional/alternative extraction should be considered. There is an abundance of the literature addressing many aspects of passive headspace extractions that should be consulted to determine optimal extraction parameters [21–25].

Dynamic Headspace Concentration

Dynamic headspace concentration employs an activated charcoal tube through which the headspace from the container is pushed or drawn [17, 26, 27]. The sample container is fitted with a modified lid or septum with an opening for intake and a second opening to attach the charcoal tube (Fig. 2.2). In positive pressure mode, a compressed gas, such as nitrogen, is pushed through the intake, forcing the headspace through the charcoal tube. In negative pressure mode, a vacuum is placed behind the charcoal tube to pull the headspace through the charcoal tube. In either mode, the container is heated (60–90 °C) and the temperature monitored. Following the extraction process, which typically ranges from 20 to 45 min, the charcoal is eluted with carbon disulfide or a suitable solvent, and the extract is then analyzed by GC-MS. A sample of the charcoal can also be preserved with the evidence in case of future analysis. Unfortunately, though this method offers a short extraction time and good sensitivity, it is very labor-intensive, requiring a lot of setup and attention from the examiner. As with passive headspace, displacement and overloading can be an issue with strong samples or under severe extraction conditions. Displacement in a dynamic system is a greater concern than in passive systems, because the displaced analyte is forever lost. In dynamic systems, this is referred to as **breakthrough** [7]. Breakthrough includes not only the displacement of previously adsorbed analyte, but also when volatile components from the headspace do not adsorb on to the adsorbent and are lost. This may occur with flow rates that are too high, saturation of the adsorbent with samples of high concentration, or excessive extraction times.

Solid-Phase Microextraction

Solid-phase microextraction (SPME) is based on the same concept as passive headspace concentration; however, the absorbent is a coated fiber rather than a charcoal strip and the desorption process is thermal rather than with a solvent [18, 28, 29]. The SPME assembly consists of the body of the device and a septum-piercing needle which is used to protect the SPME fiber inside (Fig. 2.3). The septum of the container is pierced with the needle, and the plunger is depressed to extend the fiber into the headspace of the sample. As with other adsorptive extraction techniques, the sample is heated and the adsorbent is exposed to the headspace of the sample for a period of time, typically 5–10 min. The fiber is removed from the headspace of the container and inserted in the heated GC injection port for thermal desorption and analysis. The fiber should also be analyzed prior to adsorption as a blank to ensure the fiber is free of contamination.

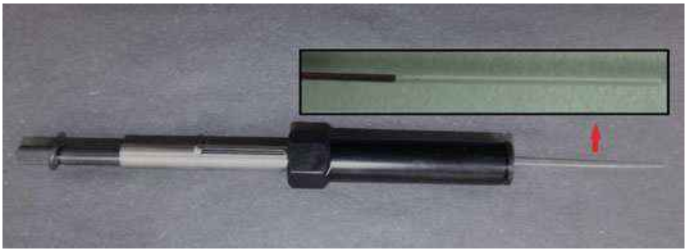


Fig. 2.3 Example of a SPME assembly with inset of the extended SPME fiber

SPME is an easy technique with little to no sample preparation, a short extraction time, and no hazardous solvents. However, the extraction and analysis have not been automated for fire debris analysis, which is not trivial, given the large number of samples routinely encountered in casework. Additionally, SPME fibers are delicate and expensive, so replacing broken fibers may be cost-prohibitive. Unlike other techniques, there is no means for archiving a sample for later analysis using SPME. As such, the ASTM standard practice for SPME recommends the use of an additional extraction technique with SPME, like passive or dynamic headspace concentration, for sample archival. Though this technique has been successfully applied to other areas of forensic science, such as blood alcohol, it remains relatively uncommon in fire debris analysis due to these concerns.

Static Headspace Concentration onto an Adsorbent Tube

Static headspace concentration onto an adsorbent tube is roughly a combination of static headspace sampling and dynamic headspace concentration. In this technique, a syringe is used to pull a sample of the headspace through an adsorbent material. Tenax®, which is a polymeric resin, is commonly used for this technique and must be thermally desorbed [30]. Static headspace concentration onto an adsorbent tube is often used internationally, but has not yet gained popularity in the USA. As of 2018, an ASTM standard practice is under development for this technique.

2.3.5 *Extraction Techniques: Solvent Extraction*

Solvent extraction is a technique in which a suitable solvent is used to isolate any potential ignitable liquids from a sample [31]. In this technique, the matrix is rinsed or soaked in a solvent. Oftentimes, solvents other than carbon disulfide are used, such as pentane or dichloromethane. Alternate solvents are preferred due to the large quantities of solvent being handled with this technique, the health hazards associated with carbon disulfide, and the fact that carbon disulfide offers no particular advantage over other nonpolar solvents, in contrast to its use as a desorption solvent. The resultant extract is then analyzed by GC-MS, though it may require filtration or concentration prior to analysis. Non-porous matrices, such as empty containers and glass fragments, are better suited for solvent extraction rather than porous materials, such as carpet or upholstery. This technique is also good for petroleum products that are of low volatility, such as lubricating oils or vegetable oils. However, this extraction technique has its disadvantages: it is considered to be destructive and labor-intensive, offers poor sensitivity, risks co-extraction of components of the matrix, and can preclude other forensic examinations such as fingerprints or DNA analysis (see Chap. 11).

2.3.6 *Instrumentation*

The gas chromatograph is the workhorse of the fire debris analysis world as it is best suited for analysis of mixtures of volatile components. Gas chromatographs equipped with a flame ionization detector (GC-FID) were common in the past and are still used in some laboratories as a screening technique; however, the GC-MS is relatively standard now in forensic science laboratories for this type of analysis. Mass spectrometers are invaluable in the identification of unknown components and are particularly useful for the complex mixtures seen with the extraction of fire debris evidence. Details on the theory of GC-MS are included in Chap. 1.

2.3.7 *Quality Control Considerations*

Regardless of extraction method, quality control measures are an important aspect of fire debris casework. A system or method blank should be prepared with each extraction to ensure that no contamination is being introduced during the extraction process. This system blank should be prepared in the same manner as the items of evidence using the same materials. For an adsorption technique, this would include the adsorbent material and any materials used for the extraction such as pipettes, paper clips, floss, or other material used to contain or suspend the adsorbent in the exhibit. For solvent extraction, any beakers or other containers that may be used in the extraction should be screened, as well as materials used for evaporation if the extract has been concentrated. For techniques requiring the use of a solvent, including adsorption methods with solvent desorption, solvent extraction, and liquid dilutions, the solvent should be analyzed to ensure it is clean. Some laboratories evaporate the solvent of choice down at the time of receipt to ensure the solvent does not have any problematic contaminants prior to use in casework.

There are also quality control checks associated with GC-MS analysis. A quality control standard and/or reference material should be run at the beginning and end of a sequence to show that the instrument is working properly. Additionally, solvent blanks should be run before every sample to show that the system is free of contamination or carryover. Some laboratories have conducted studies to show that carryover between samples is negligible and do not run solvent blanks prior to every sample. However, solvent blanks are a clear and resounding way to demonstrate that the instrument is clean.

2.4 Classification of Ignitable Liquids

Classification of ignitable liquids in fire debris analysis is based on chemical content and volatility (ease of vaporization), rather than end use [32]. In general, no attempt to identify a particular brand should be made, due to marketing and distribution practices. Alternatively, it may be helpful to an investigator to report examples of types of products within a particular ignitable liquid class, since most investigators are not trained in chemistry or in ignitable liquid classifications. This is because liquids within the same ignitable liquid class may be marketed as different types of commercial products if the properties of the liquid meet multiple end uses, such as a medium petroleum distillate being used as a charcoal starter, mineral spirits, and a paint thinner (Fig. 2.4). Also, it should be noted that different classes of ignitable liquid may be used for the same type of end use product [33]. For example, a medium petroleum distillate and a medium isoparaffinic product may both be marketed as a charcoal starter. As such, the class of ignitable liquid identified in an item of evidence is the critical piece of information for the investigator.

2.4.1 Petroleum Refining

In order to understand how ignitable liquids are classified, it is important to have a general understanding of the petroleum refining process. This section is meant to serve as only a basic and limited overview of petroleum refining. Several sources provide a much more complete and detailed description of refinery processes [34, 35]. It should be noted that terminology from petroleum refining and fire debris analysis often overlap, but do not always mean the same thing. The intent of the term used can usually be determined by the context.

Crude oil, or petroleum, is naturally occurring in the earth as a result of the decomposition of various animal and plant organisms. It is composed mainly of gaseous, liquid, and solid hydrocarbons and hydrocarbon derivatives containing oxygen, nitrogen, and sulfur as well as trace metals. **Hydrocarbons** may be further delineated as aliphatic (normal, branched, and cyclic alkanes) and aromatic compounds, though the ratios of these components vary by crude oil source. Alkanes and cycloalkanes are often referred to as paraffin and naphthenes (not to be confused with naphthalenes), respectively, by the petroleum refining industry.

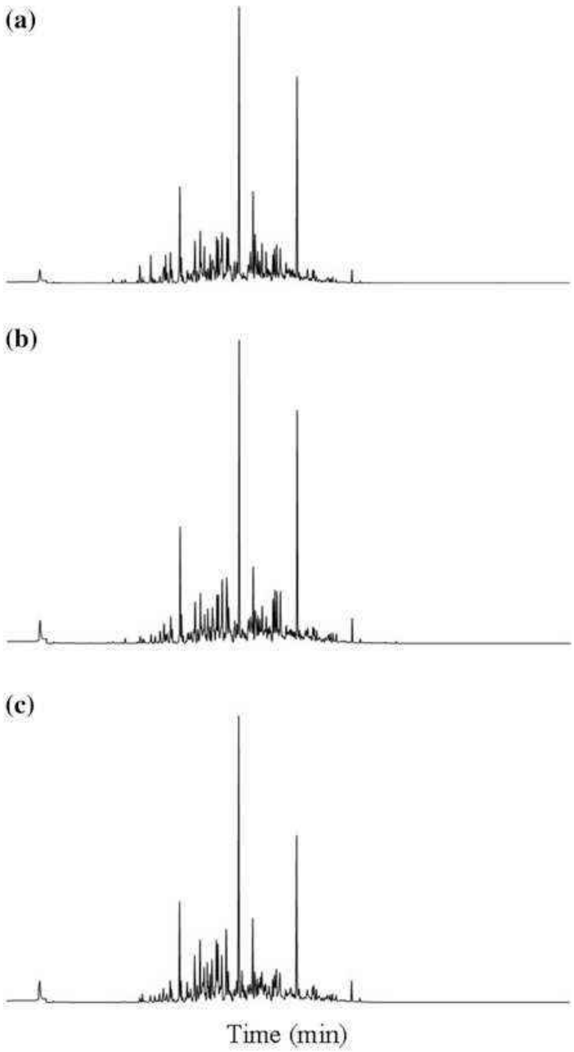


Fig. 2.4 Three different commercial products with different end uses and very similar chemical composition. **a** Charcoal starter, **b** paint thinner, and **c** mineral spirits

Generally, the overall goal of a petroleum refinery is to transform crude oil into the maximum amount of profitable fuel using chemical and physical means. Desirable products from the refinery include fuels like gasoline and kerosene, but also a wider range of petroleum products including natural gas, lubricating oils, and asphalt. The main processes that occur at the refinery include separation of components of petroleum based on boiling point (fractional distillation), changing the size of the hydrocarbons to get them into the desired boiling point range (alkylation and cracking), and changing the type of hydrocarbon (isomerization and reforming) to get components with desired properties (e.g., converting cyclic alkanes to aromatic compounds). Refineries also have processes to remove undesirable or problematic components such as sulfur or metals, which can then be separately sold by the refinery. The feedstocks from these different refinery operations may be blended together to get an end product with desired properties for particular applications.

2.4.2 Classes of Ignitable Liquids

Ignitable liquids, which may be petroleum- or nonpetroleum-based, are classified based on guidelines outlined in ASTM E1618 [32]. In this standard test method, seven ignitable liquid classes are designated, with an additional miscellaneous/other class. The majority of ignitable liquid classes describe petroleum-based ignitable liquids. Nonpetroleum-based ignitable liquids fall into the oxygenated and miscellaneous classes. As mentioned previously, classes are determined based on chemical content, particularly the presence or absence of alkane and aromatic components (Table 2.1). Alkane components may be normal, branched, or cyclic. In the context of ignitable liquids, aromatic components may be characterized as simple or polynuclear. Simple aromatics are monocyclic (benzene-based), and polycyclic aromatic compounds have multiple fused aromatic rings. The most commonly encountered polynuclear aromatic compounds in fire debris analysis are the naphthalene-based aromatic compounds. Furthermore, ignitable liquid classes may also be subcategorized as light, medium, or heavy, which indicates the boiling point range of the petroleum product.

Table 2.1 Chemical content of each class of ignitable liquid

Class of ignitable liquid	Normal alkanes	Branched alkanes	Cyclic alkanes	Simple aromatics	Polynuclear aromatics
Gasoline	Present	Present	Present	Dominant	Present
Petroleum distillate	Dominant	Present	Present	May be present (range dependent; absent if dearomatized)	May be present (range dependent; absent if dearomatized)
Naphthenic–paraffinic	May be present	Dominant	Dominant	Dominant	Absent
Isoparaffinic	Absent	Dominant	Absent	Absent	Absent
Normal alkane	Dominant	Absent	Absent	Absent	Absent
Aromatic	Absent	Absent	Absent	Dominant (range dependent)	Dominant (range dependent)
Oxygenate	Dominant presence of oxygenated component(s) (petroleum-based content may vary or be absent)				

Petroleum distillates are the least refined class of ignitable liquid. As such, the composition mirrors crude oil in a defined volatility range. Petroleum distillates contain normal alkanes, branched alkanes, and cyclic alkanes. Petroleum distillates may also contain aromatic components, though which aromatic components depend on the volatility range of the product. Petroleum distillates may also undergo specific refining processes to remove aromatic content, resulting in dearomatized distillates. Previously, dearomatized distillates were classified separately from petroleum distillates, though now all petroleum distillates (with or without aromatic content) are classified together. Petroleum distillates are used in a wide range of applications including lighter fluids, paint thinners, and diesel fuel.

Gasoline is one of the most highly refined products from the refinery due to its specific end use and desired properties. Gasoline is characterized by its enhanced aromatic content and is a blend of several refinery feedstocks. Because no classes of compounds in crude oil are specifically removed, gasoline contains both alkane and aromatic hydrocarbons from crude oil in the C_4–C_{12} range, though its overall composition is dominated by aromatic compounds.

Naphthenic–paraffinic products are similar to petroleum distillates with some additional refining. Naphthenic–paraffinic products are produced from petroleum distillates that have had aromatic components removed and normal alkane content greatly reduced or removed. As such, naphthenic–paraffinic products contain only branched and cyclic alkanes and may also contain lower levels of normal alkanes. The aromatic content is generally negligible. Like petroleum distillates, naphthenic–paraffinic products have a variety of uses including torch fuels and charcoal starters.

Isoparaffinic products are solely composed of branched alkanes. To achieve this clean product, significant refining is required. Isoparaffinic products are obtained by separating branched alkanes from normal alkanes, cyclic alkanes, and aromatic components in the isomerate feedstock. These products are generally narrow range products used in low odor products such as paint thinners and charcoal starters.

Normal alkane products are relatively self-explanatory in that they contain only normal alkanes in a specified range. These products contain only a few components and are produced by separating normal alkanes using a molecular sieve. Normal alkane products are typically in the heavy range and are used in applications that require low soot burning such as candle oils.

Aromatic products contain exclusively aromatic components in a desired range. They have no alkane content and are generally produced by solvent extraction of a feedstock that is rich in aromatic content, such as the reformate feedstock. These products are commonly used for their solvating ability in commercial products such as cleaners or specialty solvents.

Oxygenated products are those which contain a significant presence of one or more oxygenated components such as alcohols, ketones, and ethers. These products include solvents such as acetone or isopropyl alcohol, which are not derived from crude oil, and products that are a mixture of an oxygenated component with another type of petroleum product.

ASTM E1618 also includes a **miscellaneous** class that encompasses any ignitable liquids that are not described by the previous seven classes. This class covers a variety of ignitable liquids including turpentine, which is not petroleum-based, and other petroleum-based ignitable liquids that do not fit neatly into one of the aforementioned classes.

2.5 Data Interpretation

2.5.1 Pattern Recognition and Pattern Comparison

The classes of ignitable liquids are defined in terms of chemical content; however, identifying ignitable liquids using GC-MS depends on the recognition of specific patterns that are diagnostic of each class [7]. Additionally, ignitable liquids can be further classified as light, medium, or heavy, based on carbon range, which roughly equates to boiling point range. This gives the investigator an idea of the volatility of the liquid. The carbon ranges for light, medium, and heavy are C_4–C_9, C_8–C_{13}, and C_9–C_{20+}, respectively. Note that these ranges overlap and can be somewhat fluid. For example, an examiner may choose to designate an ignitable liquid ranging from C_{10} to C_{14} as medium to heavy to indicate that its volatility falls somewhere between the two ranges. Further discussion of ignitable liquid variability will be covered in Chap. 5.

Data interpretation involves **pattern recognition** and **pattern comparison**. Ignitable liquids may contain only a few components, such as n-alkane products, or dozens to hundreds of components, such as petroleum distillates. During the course of an examiner's training, numerous ignitable liquids from all classes should be analyzed by GC-MS in order to become familiar with and learn to recognize petroleum patterns. References and standards are available that demonstrate the broad range of petroleum patterns [36, 37]. Once a pattern is recognized as indicative of a petroleum product, it is compared to a reference ignitable liquid to demonstrate the consistent pattern. It should be noted that nonpetroleum-based ignitable liquids, such as oxygenated products or turpentine, generally cannot be identified using pattern recognition. These must be identified by comparison of retention times and mass spectra of constituent components to a reference.

It is important to understand that, for the majority of ignitable liquids, particularly the petroleum-based liquids, a single peak does not indicate an ignitable liquid. Rather, groups of peaks in specific ratios and patterns are used to identify ignitable liquids. There are numerous volatile components that are common to both ignitable liquids and in the pyrolysis and combustion of common household materials. This topic will be discussed in Chap. 3 [6, 7]. Therefore, the importance of pattern recognition over picking individual peaks out in a chromatogram cannot be overstated.

2.5.2 Extracted Ion Profiles

Typically, diagnostic patterns are first observed in the **total ion chromatogram (TIC)**, which is a sum of the entire signal produced by the mass spectrometer. **Extracted ion profiles (EIPs)** are also used to highlight specific chemical classes, such as the alkane or aromatic content in a sample. EIPs are constructed by selecting a group of ions (*m/z* ratios) and plotting the sum of only their signal, rather than the entire signal as is done for the TIC. These ions can be viewed singly as extracted ion chromatograms (EICs), though often the sum as shown in the EIP gives a better overall picture of the entire class of compounds. It is important to note that peaks outside the chemical class of interest may appear in an EIP. For example, nonane and decane are often seen in the polynuclear aromatic EIP since they have ions in their mass spectra that are included in that profile. These peaks should not be considered part of a characteristic pattern in the EIP. Table 2.2 gives common groups of ions used to visualize the alkane, cycloalkane/alkene, simple aromatic, indane, and polynuclear aromatic (PNA) content in ignitable liquids. It is important to understand that no one single EIP should be used on its own to identify an ignitable liquid; it must be used in context with other EIPs and the TIC.

2.5.3 Diagnostic Patterns: Petroleum Distillates

A major diagnostic pattern is a Gaussian pattern of spiking n-alkanes with lower branched and cyclic alkane content, which is indicative of petroleum distillates. This pattern can be observed in the total ion chromatogram and the alkane EIP. The shape and breadth of the pattern depend on the carbon range of the product. Medium and heavy petroleum distillates (MPD, HPD) have a clear bell-curve shape, with heavy petroleum distillates tending to span a broader carbon range. The shape of the bell curve for light petroleum distillates (LPDs) may not be as clear as medium or heavy petroleum distillates. Due to the volatility of LPDs, the left side of the curve may be missing as those components are generally too light to appear in a chromatogram under typical conditions. Additionally, it is common to see a relatively high abundance of branched and cyclic components in these products, compared to medium or heavy distillates, as there are fewer isomers for the smaller hydrocarbons in the light range. Figure 2.5 shows an example of a light, medium, and heavy petroleum distillate.

Table 2.2 Ions summed to create each extracted ion profile (EIP)

Chemical class	EIP (m/z)
Alkane	57, 71, 85, 99
Cycloalkane/alkene	55, 69, 83, 97
Simple aromatic	91, 105, 119, 133
Indane	117, 131, 145
Polynuclear aromatic	128, 142, 156

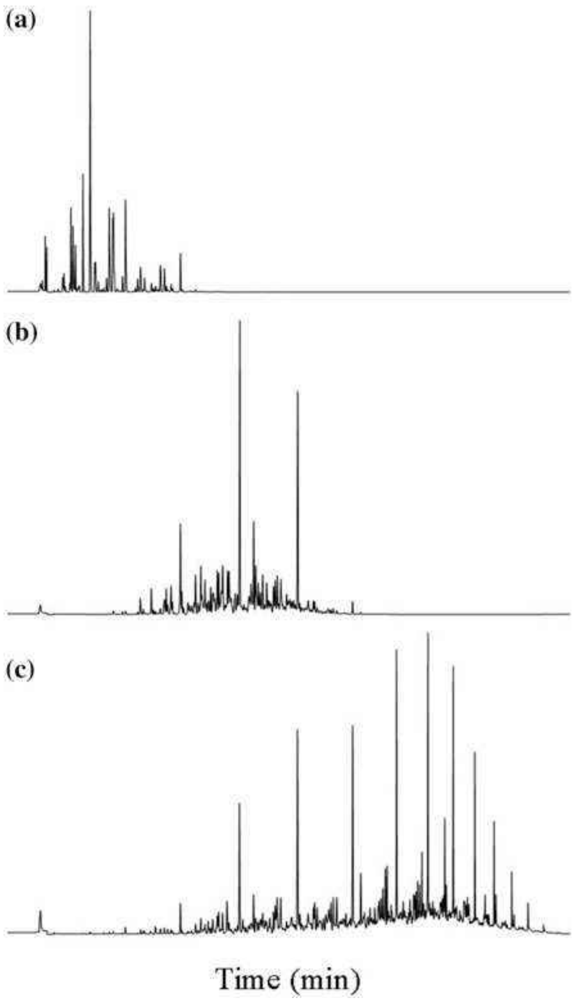


Fig. 2.5 TIC of a light (**a**), medium (**b**), and heavy (**c**) petroleum distillate

2.5.4 Diagnostic Patterns: Gasoline (and Aromatic Products)

Gasoline has a very recognizable pattern of aromatic components necessary for its identification. As stated previously, gasoline is characterized by dominant aromatic content ranging from toluene through the C_4-alkylbenzenes. The ratios of the aromatic compounds within each group of alkylbenzenes and between the groups are key in the identification of gasoline. The pattern can be observed in the TIC and the aromatic EIP in Fig. 2.6. Though the pattern of the aromatic content in gasoline gets the most attention, patterns in the other EIPs need to be considered as well. The indane and PNA EIPs also have diagnostic petroleum patterns. While these patterns

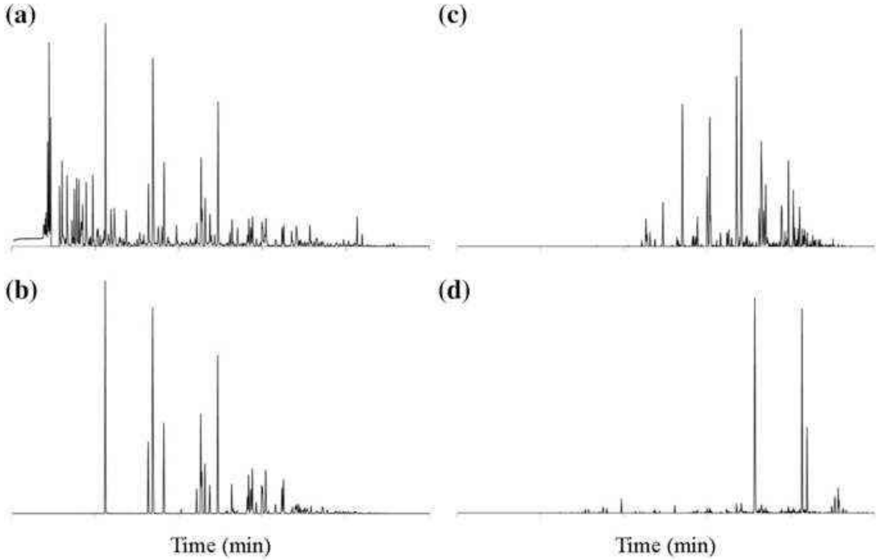


Fig. 2.6 TIC (**a**), aromatic EIP (**b**), indane EIP (**c**), and polynuclear aromatic EIP (**d**) of gasoline

are not exclusive to gasoline, they are considered indicative of a petroleum product and may be present in any petroleum product within a given range. The alkane EIP is also important in identifying gasoline, as the presence of alkane content separates gasoline from an aromatic product. The alkane content varies greatly from one gasoline to another and can be similar to a distillate or isoparaffinic pattern in the alkane EIP. Additionally, gasoline often contains ethanol (up to 10%), which is added to enhance the octane rating [35].

It is important to note that the aromatic patterns seen in gasoline are also the same patterns seen in aromatic products. As opposed to gasoline, aromatic products generally have a narrow range which may only cover toluene and xylenes or only the C_3-alkylbenzenes, depending on the cut (Fig. 2.7). The ratios within the groups of alkylbenzenes will be similar to those seen in gasoline, though ratios between groups may vary. With this similarity in mind, alkane content and overall breadth of the aromatic pattern are critical in differentiating these two classes.

2.5.5 Diagnostic Patterns: Isoparaffinic and Naphthenic–Paraffinic Products

Though isoparaffinic and naphthenic–paraffinic products are not traditionally considered to have diagnostic patterns, petroleum patterns indicative of these classes can be just as recognizable as a Gaussian curve in petroleum distillates or aromatic content in gasoline. Both classes are characterized by their alkane content and have

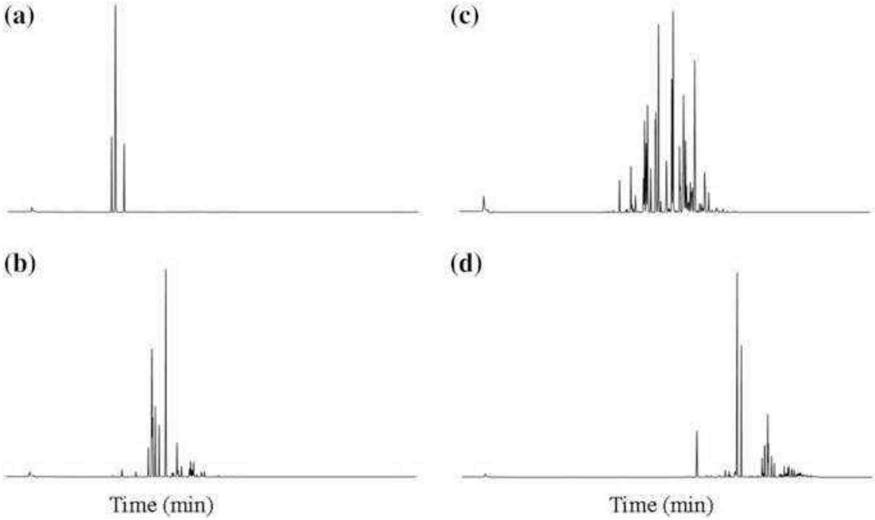


Fig. 2.7 TIC of four different aromatic products ranging from light to heavy

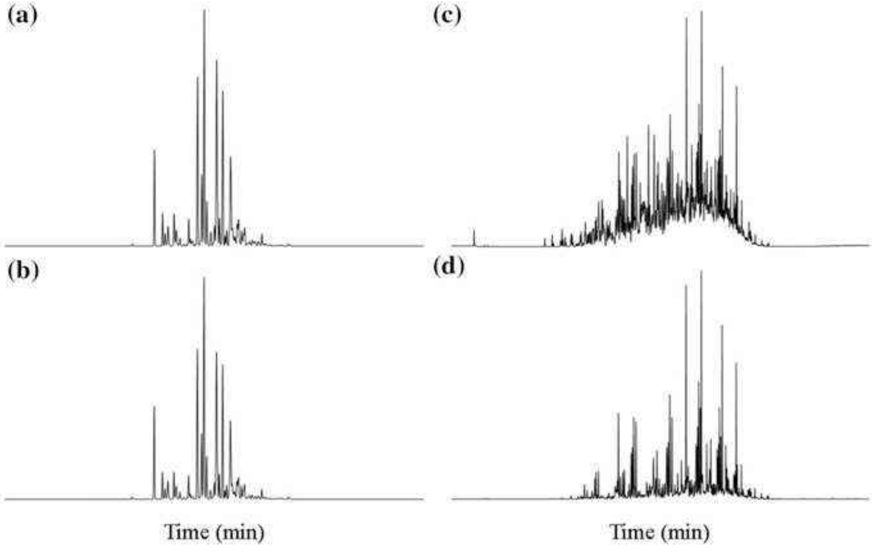


Fig. 2.8 Isoparaffinic product TIC (**a**) and alkane EIP (**b**) showing very similar patterns and naphthenic–paraffinic product TIC (**c**) and alkane EIP (**d**) showing a pattern of petroleum branching similar to a petroleum distillate

reduced or removed aromatic content. The alkane and cycloalkane EIPs can be helpful in identifying these classes [Fig. 2.8]. The alkane and cycloalkane EIPs for isoparaffinic products are nearly identical to each other and the TIC, with the only notable difference being the abundance. Oftentimes, naphthenic–paraffinic products look similar to petroleum distillates, with the spiking n-alkanes missing or greatly reduced. This resemblance is often more obvious in the alkane EIP than in the TIC. For both classes, heavy products are typically unresolved envelopes due to the large number of isomers for larger hydrocarbons.

2.5.6 Mixtures

An ignitable liquid may contain more than one recognizable petroleum pattern. A mixture may be the result of the presence of two different commercial products or may be a single product that contains a blend of more than one class of ignitable liquid. For example, Fig. 2.9 shows a commercial product that is a mixture of a

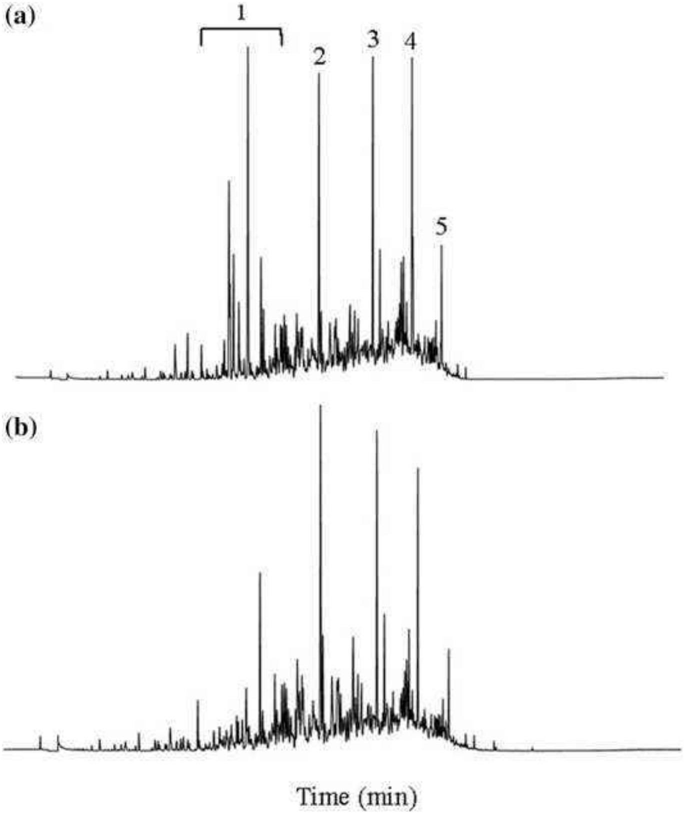


Fig. 2.9 TIC of a commercial product that contains a medium aromatic product and a medium-to-heavy petroleum distillate (**a**), compared to a more traditional petroleum distillate (**b**). (1) C_3-alkylbenzenes, (2) undecane, (3) dodecane, (4) tridecane, (5) tetradecane

medium aromatic product and a heavy petroleum distillate compared to a product that only contains a heavy petroleum distillate. A petroleum distillate may contain C_3-alkylbenzenes, (depending on the range of the distillate and if it is not dearomatized); however, the abundance of the aromatic pattern in a distillate is lower than the alkane content. When the relative abundance of the aromatic content increases above the level that can be expected in a petroleum distillate, the examiner may consider the presence of a mixture. If each pattern is sufficiently distinct, both patterns may be identified. However, due to the overlap of components in all ignitable liquids, identification of mixtures should be approached with caution.

Reporting of mixtures may vary between laboratories. Some laboratory protocols allow an examiner to identify the presence of both classes of ignitable liquid in a sample. In order to help the investigator in understanding the results, a qualifying statement should be included to indicate that the mixture may be a result of multiple ignitable liquids or a single commercial product. An example of such a qualifier for the product shown in Fig. 2.9 is provided below:

> Exhibit 1 contained a medium aromatic product and a heavy petroleum distillate. It could not be determined if Exhibit 1 contained two individual products or a single commercial product.

Conversely, some laboratory protocols may require such mixtures to be reported as a miscellaneous product. Though this option is acceptable, the identification of each component in the mixture, rather than grouping them together as a miscellaneous product, may provide better and more detailed information for the investigators. A miscellaneous classification is not specific for the investigator, whereas listing each class separately may provide a lead. In addition, reporting a miscellaneous product could imply a single commercial product and potentially be misleading.

2.5.7 Single Components

Not all ignitable liquids are complex mixtures that can be identified using pattern recognition and pattern comparison. Ignitable liquids that consist of a single or very few components are identified by comparing retention times and mass spectra to a reference liquid or standard. Nonpetroleum-based ignitable liquids such as oxygenated compounds/solvents (ethanol, isopropanol, and methyl ethyl ketone, to name a few) and terpenes are identified in this way. It should be noted that terpenes are naturally occurring in some woods and a discussion of their identification is included in Chap. 3. Caution should be exercised when identifying single components as many components of interest, such as acetone or toluene, may also originate from the matrix (see Chap. 3). Many examiners find it useful to use a rule of thumb for identification, wherein the single component should be greater than the abundance of the matrix peaks by a factor of 10 for identification.

Identification using retention times and mass spectra should also be considered when identifying classes of ignitable liquids that typically have very few components since these liquids do not have a sufficient pattern to use for pattern recognition. Some examples of classes that may require single component identification include n-alkane and some aromatic products.

2.5.8 Complications in Data Interpretation

So far, the discussion and figures in this section have concerned the identification of neat ignitable liquids. The identification of ignitable liquid residues extracted from a matrix such as fire debris or clothing is often much more complex. There are multiple issues that complicate this type of data interpretation including evaporation/weathering of ignitable liquids, co-extraction of interfering volatile components from a matrix, ignitable liquids inherent to a particular matrix, and microbial degradation of petroleum products. These issues are covered in detail in Chaps. 3, 5, and 6.

2.6 Other Fire Debris Examinations

Occasionally, examinations or analyses outside of typical ignitable liquid testing will be requested of a fire debris examiner. These examinations may include analysis of lubricating oils, vegetable oils, and incendiary devices.

2.6.1 Lubricating Oils

Lubricating oils potentially fall under the scope of a fire debris examination because they are petroleum products. Lubricating oils come from a heavy boiling fraction of crude oil and generally contain an unresolved envelope of hydrocarbons ranging from C_{18} to C_{40+} [35]. There are multiple types of lubricating oils including conventional lubricating oils from crude oil, synthetic lubricating oils that are modified petroleum products, and synthetic blends, which are mixtures of conventional and synthetic lubricating oils (Fig. 2.10). Additional components such as glycols and esters may be added to some lubricating oils to alter their properties. Unlike ignitable liquids, lubricating oils are not generally detected using typical headspace methods as they are not volatile. A solvent extraction should be performed after routine ignitable liquid or explosive analysis if a lubricating oil is suspected. Though some components of lubricating oils can be observed using a typical GC-MS, a high-temperature instrument (HTGC-MS) is preferred for identification of heavier oils [38–40]. Lubricating oils should be compared to a

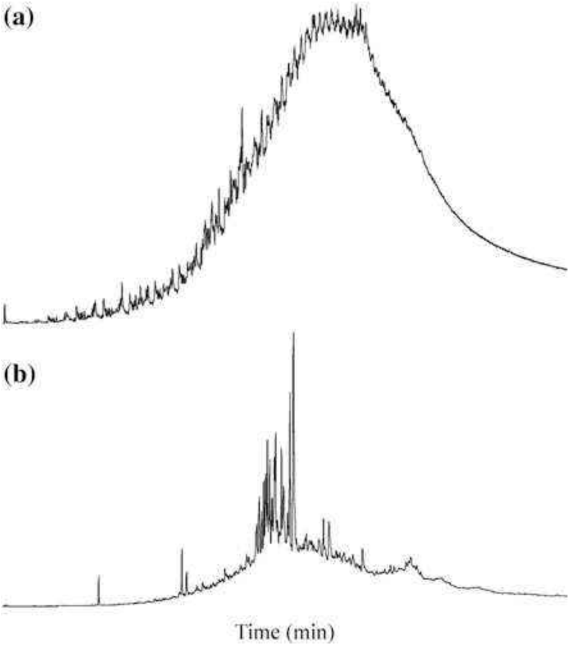


Fig. 2.10 Examples of a conventional (**a**) and synthetic (**b**) lubricating oil

reference lubricating oil for identification. Features for comparison include carbon range, unresolved envelope shape, and location of the maximum of the unresolved envelope.

Questioned and known lubricating oils may be compared using HTGC-MS, which requires a special injection port (programmable temperature vaporization), column (typically aluminum or polyimide-clad), and temperature program (reaching temperatures above 350 °C). For example, Fig. 2.11 shows the comparison of a questioned lubricating oil found in an incendiary device to two lubricating oils recovered from a suspect's house. The lubricating oil from the scene and one of the oils from the suspect's house were found to be similar in chemical composition based on carbon range, envelope shape, and envelope maximum and therefore could have originated from the same source or another source with the same chemical composition.

2.6.2 Vegetable Oils

Vegetable oils are increasingly included in fire debris analysis due to the propensity of some oils to self-heat, which may lead to spontaneous ignition and cause a fire [41–44]. Vegetable oils are composed of triglycerides, which are three fatty acids connected by a glycerol backbone. Vegetable oils are prone to self-heating when

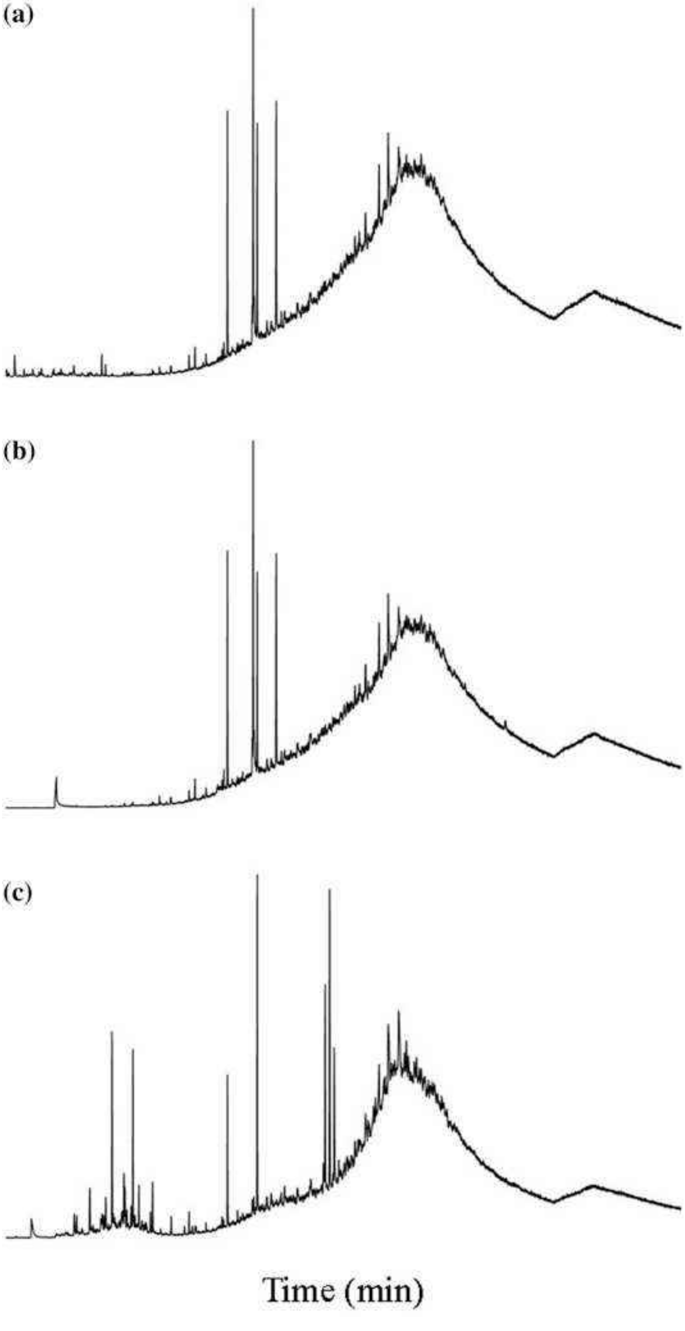


Fig. 2.11 Comparison of a lubricating oil extracted from the debris of an incendiary device (**a**) and two lubricating oils recovered from the suspect (**b, c**) analyzed by HTGC-MS

they have a large percentage of polyunsaturated fatty acids. Examples of vegetable oils that are prone to self-heating include linseed oil and tung oil, which are commonly used as drying oils and wood finishes.

Because of this difference in chemical composition from petroleum-based ignitable liquids, different methods of analysis need to be used. Vegetable oils are isolated from fire debris using solvent extraction rather than a headspace technique. When analyzing a neat vegetable oil, the oil is diluted in pentane or other suitable solvent. Because triglycerides and free fatty acids in vegetable oils are not well suited for analysis by GC-MS, the solvent extract or diluted liquid is derivatized to form fatty acid methyl esters (FAMEs), which are more easily analyzed by GC-MS [45]. Further background information and guidance on extraction and analysis of vegetable oils can be found in Chap. 4.

2.6.3 Incendiary Devices

An **incendiary device** is a device that is designed to start or communicate a fire. There are many effective device constructions available to would-be arsonists, and it is important for an examiner to be somewhat familiar with the most common types. The simplest and perhaps most common incendiary device is a Molotov cocktail. A Molotov cocktail is assembled by filling a breakable container with an ignitable liquid and inserting a wick. More complicated devices are relatively rare. Analysis of incendiary devices should include screening for ignitable liquids as well as a thorough description of all of the components that make up the device. Additional instrumental analysis, such as FTIR or SEM-EDS, may be necessary to characterize components of the device.

Additionally, when analyzing an incendiary device, the examiner should consider the wealth and variety of evidence that may be present and coordinate with examiners from other disciplines. Components of incendiary devices are often great sources of fingerprint, DNA, or trace evidence (see Chap. 11). Additionally, some devices may be a combination of both ignitable liquids and explosives.

It should be noted that incendiary devices, particularly Molotov cocktails, pose a packaging challenge for investigators. Any devices or components that are to be analyzed for ignitable liquids must be packaged in vapor-tight packaging. While breathable packaging is preferable for fingerprints and DNA, vapor-tight packaging is required for fire debris analysis. If the Molotov cocktail is intact, a sample of liquid should be removed from the bottle for ignitable liquid analysis. The remaining liquid in the bottle can be discarded and the bottle dried and packaged for fingerprints and DNA. The wick of the Molotov may then be packaged in a can to preserve any ignitable liquids. Depending on the material used for the wick, it may also be examined for DNA and even fingerprints. If the Molotov cocktail has been deployed, the fragments of glass and wick should be packaged separately in vapor-tight packaging to avoid contact between the glass and the wick which may impact the recovery of DNA or fingerprints. Packaging for other types of incendiary devices should be considered on a case-by-case basis.

2.7 Reporting Results

2.7.1 General Reporting Guidelines

At the conclusion of a fire debris examination, the examiner will issue a scientific report of the results. The report should detail the items of evidence analyzed and the results for each item. Usually, the results consist of identifying the presence or absence of an ignitable liquid. If an ignitable liquid is present, the class should be reported. The volatility range may also be included by designating the class as light, medium, or heavy. Sometimes, the report may also include a detailed physical description of the evidence. This type of result is particularly of interest for incendiary devices where description of device components may help link multiple devices or assist in the execution of a search warrant.

It should be noted that this report is intended for the investigator who submitted the evidence and the content and wording of the report should reflect this audience. The investigator likely only has a basic chemistry background and limited knowledge of petroleum products and refining. When reporting the class of ignitable liquid, it is often helpful to the investigator to list some examples of commercial products of this class (e.g., some examples of medium petroleum distillates include some paint thinners and charcoal starters). However, results should never report an item as containing a specific commercial product. As mentioned previously, petroleum products of the same class could be marketed as a wide variety of commercial products with different end uses. Along the same lines, a single component should be reported with examples of common uses or sources to help the investigator better understand the context and significance of the result.

Additionally, the examiner should not use misleading or unclear terminology in the report. For example, a report should never include the words “hydrocarbon(s)” or “volatile component(s)” as they are non-specific and not indicative of or exclusive to petroleum products, nor should the report include phrasing such as “components consistent with,” “in the boiling range of,” or “characteristic of,” as their intent is unclear to the investigator, particularly if no ignitable liquid class is being reported. This may lead to a confused investigator wondering if an ignitable liquid was really present. Terms such as “residue,” “evaporated,” or “weathered” may be used to describe the condition of the ignitable liquid recovered, though “fire-aged” should be avoided as it implies that this condition is the result of a fire, which may or may not be true. As mentioned previously, ignitable liquids should never be referred to as “accelerants” as that term implies intent rather than an objective result.

2.7.2 Qualifying Statements

The presence of ignitable liquids in evidence is not, in itself, an indication of an incendiary fire, nor is the absence an indication of a natural or accidental fire. There are multiple legitimate reasons for an ignitable liquid to be present: gasoline found in a garage fire or a medium petroleum distillate (often in paint thinners) found in an art studio. Conversely, there are several reasons for a particular item to be reported as not containing an ignitable liquid: the ignitable liquid was completely consumed in the fire, ignitable liquids were present at the scene, but not in the specific item that was collected, or possibly ignitable liquids were indicated in the GC-MS data, but the signal or pattern was not clear or strong enough for identification.

Some laboratories include qualifying statements in their reports to give an additional perspective to the results. These statements should be used with caution as it is generally considered to be beyond the scope of the examiner's role to determine the reason that an ignitable liquid may be present or absent. Also, these statements may produce the appearance of bias, particularly if a qualifying statement is only provided for negative results. An acceptable qualifying statement would give possible reasons for both positive and negative results. ASTM E1618 provides examples of a qualifying statement for positive and negative results [32]:

> Positive results: The identification of an ignitable liquid residue in a fire scene does not necessarily lead to the conclusion that a fire was incendiary in nature. Further investigation may reveal a legitimate reason for the presence of ignitable liquid residues.
>
> Negative results: The absence of an ignitable liquid residue does not preclude the possibility that ignitable liquids were present at the fire scene. Ignitable liquids are volatile compounds that may have evaporated, been totally consumed in a fire, environmentally altered or removed, or may be otherwise indistinguishable from background materials.

2.8 Questions

1. What are common types of packaging for fire debris analysis?
2. Why are ignitable liquids classified and not brand identified?
3. What is the goal of the petroleum refinery?
4. How are ignitable liquids classified? Describe each class.
5. Explain the two components of data interpretation.
6. What are comparison samples and why should comparison samples collected be the same as the material of interest?
7. Why are lubricating oils and vegetable oils potentially included in fire debris analysis?
8. What is an incendiary device? Describe how to package an intact Molotov cocktail.
9. Why should fire debris examiners avoid terms such as “arson” and “accelerant”?

References

1. An Overview of the US Fire Problem (2017) National Fire Protection Association. https://www.nfpa.org/-/media/Fires/News-and-Research/Fire-statistics/Fact-sheets/FireOverviewFactSheet.pdf. Accessed 09 June 2018
2. Sandercock PML (2017) A survey of fire debris casework in Canada, 2011–2016. Can Soc For Sci J 45:64–78. https://doi.org/10.1080/00085030.2017.1380979
3. NFPA® 921 (2017) Guide for fire and explosion investigations, 2017 edn. National Fire and Protection Association
4. De Haan JD, Icove, DJ (2011) Kirk's fire investigation, 7th edn. Pearson, London
5. Baerncopf J, Anuszczyk C (2016) Comparing the response of portable hydrocarbon detectors to laboratory analysis of household substrates. Fire Arson Invest 66(4):16–21
6. Lentini JJ, Dolan JA, Cherry C (2000) The petroleum-laced background. J Forensic Sci 45(5): 968–989
7. Stauffer E, Dolan J, Newman R (2008) Fire debris analysis. Elsevier Inc, Burlington
8. Williams MR, Sigman M (2007) Performance testing of commercial containers for collection and storage of fire debris evidence. J Forensic Sci 52(3):579–585
9. Schwenk L (2014) Evidence packaging for fire debris: why vapor-tight containers matter. Fire Arson Invest 64(4):24–27
10. ASTM E1492-11(2017) Standard practice for receiving, documenting, storing, and retrieving evidence in a Forensic Science Laboratory. ASTM International, West Conshohocken, PA, www.astm.org
11. ASTM E1459-13 (2013) Standard guide for physical evidence labeling and related documentation. ASTM International, West Conshohocken, PA, www.astm.org
12. Gambrel AK, Reardon MR (2008) Extraction, derivatization, and analysis of vegetable oils from fire debris. J Forensic Sci 53(6):1372–1380
13. Kassin SM, Dror LE, Kukucka J (2013) The forensic confirmation bias: problems, perspectives, and proposed solutions. J Appl Res Mem Cogn 2:42–52
14. Butt L (2013) The forensic confirmation bias: problems, perspectives, and proposed solutions —commentary by a forensic examiner. J Appl Res Mem Cogn 2:59–60
15. Caddy B, Smith FP, Macy J (1991) Methods of fire debris preparation for detection of accelerants. Forensic Sci Rev 3(1):58–69
16. ASTM E1388-17 (2017) Standard practice for static headspace sampling of vapors from fire debris samples. ASTM International, West Conshohocken, PA, www.astm.org
17. ASTM E1412-16 (2016) Standard practice for separation of ignitable liquid residues from fire debris samples by passive headspace concentration with activated charcoal. ASTM International, West Conshohocken, PA, www.astm.org
18. ASTM E1413-13 (2013) Standard practice for separation of ignitable liquid residues from fire debris samples by dynamic headspace concentration. ASTM International, West Conshohocken, PA, www.astm.org
19. ASTM E2154-15a (2015) Standard practice for separation and concentration of ignitable liquid residues from fire debris samples by passive headspace concentration with solid phase microextraction (SPME). ASTM International, West Conshohocken, PA, www.astm.org
20. ASTM E2451-13 (2013) Standard practice for preserving ignitable liquids and ignitable liquid residue extracts from fire debris samples. ASTM International, West Conshohocken, PA, www.astm.org
21. Dietz WR (1991) Improved charcoal packaging for accelerant recovery by passive diffusion. J Forensic Sci 36(1):111–121
22. Newman RT, Dietz WR, Lothridge K (1996) The use of activated charcoal strips for fire debris by passive diffusion. Part 1: The effects of time, temperature, strip size, and sample concentration. J Forensic Sci 41(3):361–370

23. Williams MR, Fernandes D et al (2005) Adsorption saturation and chromatographic distortion effects on passive headspace sampling with activated charcoal in fire debris analysis. J Forensic Sci 50(2):316–325
24. Phelps JL, Chasteen CE, Render MM (1994) Extraction and analysis of low molecular weight alcohols and acetone from fire debris using passive headspace concentration. J Forensic Sci (39(1):194–206
25. Demers-Kohl JF, Ouderkirk SL et al (1994) Evaluation of the DFLEX® device for fire debris analysis. Can Soc Forensic Sci J 27(3):99–123
26. Saferstein R, Park SA (1982) Application of dynamic headspace analysis to laboratory and field arson investigations. J Forensic Sci 27(3):484–494
27. Sandercock PML (1994) Comparison of passive charcoal adsorption with a dynamic charcoal adsorption technique. Can Soc Forensic Sci J 27(3):179–201
28. Furton KG, Bruna J (1995) A simple inexpensive, rapid, sensitive, and solventless technique for the analysis of accelerants in fire debris based on SPME. J High Resol Chromatogr 18:625–629
29. Furton KG, Almirall JR, Bruna JC (1996) A novel method for the analysis of gasoline from fire debris using headspace solid-phase microextraction. J Forensic Sci 41(1):12–22
30. Buchem BV (2018) Tenax® https://www.buchem.com/. Accessed 09 June 2018
31. ASTM E1386-15 (2015) Standard practice for separation of ignitable liquid residues from fire debris samples by solvent extraction. ASTM International, West Conshohocken, PA, www.astm.org
32. ASTM E1618-14 (2014) Standard test method for identification of ignitable liquid residues in extracts from fire debris samples by gas chromatography-mass spectrometry. ASTM International, West Conshohocken, PA, www.astm.org
33. Baerncopf J, Hutches K (2014) A review of modern challenges in fire debris analysis. Forensic Sci Int 244:e12–e20
34. Leffler WL (2000) Petroleum refining in nontechnical language, 3rd edn. PennWell Corporation, Tulsa
35. Gary JH, Handwerk GE, Kaiser JK (2007) Petroleum Refining Technology and Economics, 5th edn. CRC Press, Boca Raton
36. Newman R, Gilbert M, Lothridge K (1998) GC-MS guide to ignitable liquids. CRC Press, Boca Raton
37. Ignitable Liquids Database (2018) National Center for Forensic Science, University of Central Florida. https://ilrc.ucf.edu. Accessed 09 June 2018
38. Reardon MR, Allen L, Bender EC, Boyle KM (2007) Comparison of motor oils using high-temperature gas chromatography-mass spectrometry. J Forensic Sci 52:656–663
39. Reardon MR, Bender EC (2005) Differentiation of composition of C-4 based on the analysis of process oil. J Forensic Sci 50:564–570
40. Hibbard R, Goodpaster JV, Evans MR (2011) Factors affecting the forensic examination of automotive lubricating oils. J Forensic Sci 56:741–753
41. Stauffer E (2005) A review of the analysis of vegetable oil residues from fire debris samples: spontaneous ignition, vegetable oils, and the forensic approach. J Forensic Sci 50:1090–1100
42. Stauffer E (2005) A review of the analysis of vegetable oil residues from fire debris samples: analytical scheme, interpretation of the results, and future needs. J Forensic Sci 51:1016–1032
43. Gambrel AK, Reardon MR (2008) Extraction, derivatization, and analysis of vegetable oils from fire debris. J Forensic Sci 53:1372–1379
44. Schwenk LM, Reardon MR (2009) Practical aspects of analyzing vegetable oils in fire debris. J Forensic Sci 54:874–880
45. ASTM E2881-13e1 (2013) Standard test method for extraction and derivatization of vegetable oils and fats from fire debris and liquid samples with analysis by gas chromatography-mass spectrometry. ASTM International, West Conshohocken, PA, www.astm.org

Jamie Baerncopf is Forensic Chemist in the Bureau of Alcohol, Tobacco, Firearms, and Explosives, specializing in fire debris and trace evidence analysis. She has published fire debris related research in scientific journals including Journal of Forensic Sciences, Forensic Science International, and Fire and Arson Investigator and presented at local and national forensic science conferences.

Sherrie Thomas is Forensic Chemist in the Bureau of Alcohol, Tobacco, Firearms and Explosives. She specializes in fire debris analysis. For over 20 years, she has instructed laboratory capabilities at the Federal Law Enforcement Training Center (FLETC) and served as Test Administrator for the Alcohol, Tobacco, Firearms and Explosives' Arson Detection Canine Program. Her accomplishments include serving on the National Response Team for 20 years.

Chapter 3
Background Interference in Fire Debris Analysis

P. Mark L. Sandercock

Learning Objectives

- Learn why is it important to be aware of the types of volatile and semi-volatile compounds present in burned and unburned substrates.
- Understand the three different mechanisms by which background or potentially interfering compounds in fire debris samples may arise: pyrolysis, combustion, and distillation.
- Understand the different sources of potentially interfering compounds encountered in fire debris analysis.
- Become familiar with the three main pathways or mechanisms, by which pyrolysis products are formed from polymers.
- Understand the importance of generating pyrolysis data from a variety of burned and unburned substrates, and how this data assists in identifying which compounds extracted from a sample of fire debris originated from the substrate and which came from an ignitable liquid.

3.1 Introduction

As discussed in Chap. 2, the forensic analysis of fire debris normally consists of headspace extraction of volatiles from the debris onto activated carbon [1, 2] or using solvent extraction [3], followed by analysis using gas chromatography–mass spectrometry (GC-MS) [4]. It should be re-emphasized that solvent extraction will recover a wider range of compounds, both volatile and semi-volatile. Regardless of whether headspace or solvent extraction is employed, fire debris will often contain a plethora of compounds that originate from the substrate (e.g., carpet, wood, vinyl flooring, clothing, furniture, etc.) removed from the scene. If an ignitable liquid is

---

P. M. L. Sandercock (✉)
Retired, Royal Canadian Mounted Police, Edmonton, AB, Canada

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_3

also present in the fire debris sample, then compounds from both substrate and ignitable liquid will appear together in the chromatogram.

In fire debris analysis, the presence of any volatile compounds in the sample that may interfere with the identification of an ignitable liquid is known as the **background**. These volatile background compounds often originate from the pyrolysis and combustion of material at the fire scene. In addition, volatile compounds such as terpenes from softwoods, the products of human perspiration in clothing, or traces of solvent that remain after the application of a furniture or floor finish may be found in *unburned* substrates. These volatiles are observed in the analysis of fire debris as a background profile in the resulting chromatogram and, depending on the types of compounds and their concentration, can interfere with the identification of an ignitable liquid. These interfering background compounds are commonly present in fire debris samples, so it is important for the fire debris examiner to understand their origin and which compounds comprise the background so that a proper interpretation of the chromatographic data and correct identification of any ignitable liquids may be made [5, 6].

In general, background compounds in fire debris samples may arise via three different mechanisms: pyrolysis, combustion, and distillation. **Pyrolysis**, the thermal degradation of organic compounds, has long been recognized by forensic scientists as the mechanism by which volatiles are generated from burning substrates (e.g., wood joists, plywood subfloor, flooring materials, and furnishings) at the fire scene [7]. Technically, pyrolysis is a chemical reaction caused by the application of thermal energy (heat) in the absence of oxygen [8]. Pyrolysis acts on organic compounds to form new compounds and is often considered to be a degradation process where larger molecules are broken down into smaller ones. In structure fires, thermal degradation in low oxygen environments may be considered a form of pyrolysis. **Combustion** is the thermal reaction of organic compounds in the presence of oxygen, which under ideal conditions will produce only carbon dioxide and water. More typically at a fire scene, however, incomplete combustion will occur, resulting in the formation of new compounds [9, 10]. Combustion may also be thought of as “oxidative pyrolysis” [8]. **Distillation** is the process, whereby volatile organic compounds are released or extracted from a material by the application of heat. A common example of distillation at a fire scene is the release of various terpenes from burning softwood [11], a material often used in residential wood frame construction, which may then condense and concentrate on cooler materials at the scene. In practice, all three processes will occur simultaneously at a fire scene and so interfering compounds from all three processes may be present in a sample of fire debris.

3.2 Interference from Burned Materials at the Fire Scene

The vast majority of interfering compounds encountered during the analysis of fire debris samples will arise from materials that have been burned. Residential (single-family dwellings, apartments, etc.) and commercial (i.e., office building, factories, etc.) structures, as well as motor vehicles, are made from a wide variety of materials, both naturally occurring (i.e., wood) and synthetic (i.e., plastics), that are capable of burning. Conditions during the fire, including heating rate, temperature range, and the availability of oxygen, will result in pyrolysis and incomplete combustion of the materials present and in some cases distillation, which in turn will give rise to many different volatile compounds. These compounds may then condense on cooler surfaces at the scene—such as flooring—or become adsorbed onto cooler, nonflammable materials such as fiberglass insulation. The presence of these compounds, particularly in high concentrations, may interfere with the detection and identification of an ignitable liquid that was added to the scene by an arsonist to accelerate the fire. Some of these interfering compounds may be the same as those present in some ignitable liquids, which may lead to the false-positive identification of an ignitable liquid if the full pattern of the ignitable liquid, including relative ratios of compounds within a group, is not taken into account.

3.2.1 Wood

In North America, wood accounts for a large proportion of the building material used by the construction industry. Often used in the construction of residential dwellings—from single-family homes to multi-story condominiums—wood is used as structural support and may also be found in subfloors, studs, joists, and trusses, as well as in exterior applications such as cladding, doors, window frames, porches, and decks. Wood is also commonly used as an interior finish in buildings and may be used for flooring, baseboard, cabinetry, interior doors, etc. As a result, samples of wood are often collected at fire scenes to help determine whether or not the fires were the result of arson.

The structure of wood consists mainly of two natural polymers: cellulose and lignin. Cellulose, which is a polysaccharide (i.e., a polymeric carbohydrate), is the structural component of plants. It is the most abundant polymer in wood, constituting approximately 50% of dry wood by weight [12]. Lignin, a network of phenolic compounds, is the second most abundant material in wood. It makes up approximately 23–33% of dry softwoods and 16–25% of hardwoods, by weight [12].

Pyrolysis of wood will cause a large number of volatile organic compounds to be formed. One of the most comprehensive lists of thermal degradation products from wood was published by Faix et al. Faix catalogued electron impact data for 82 monomeric lignin-derived degradation products, many of which are alkylated phenols [13, 14], and 104 polysaccharide (i.e., cellulose)-derived compounds [15, 16], many of which were alcohols, aldehydes, esters, and furans.

The pyrolysis of cellulose proceeds via depolymerization to form the anhydro-monosaccharide levoglucosan (an anhydrous hexose) [17], which may then rearrange into various other anhydro-monosaccharides [18]. Although it is not clear if depolymerization occurs via an ionic or free radical mechanism [17], levoglucosan is formed via random cleavage of the bonds in the cellulose polymer backbone (known as random chain scission). Specifically, the bond between carbon C1 and the hydroxyl oxygen atom attached to carbon C6 occurs (Fig. 3.1).

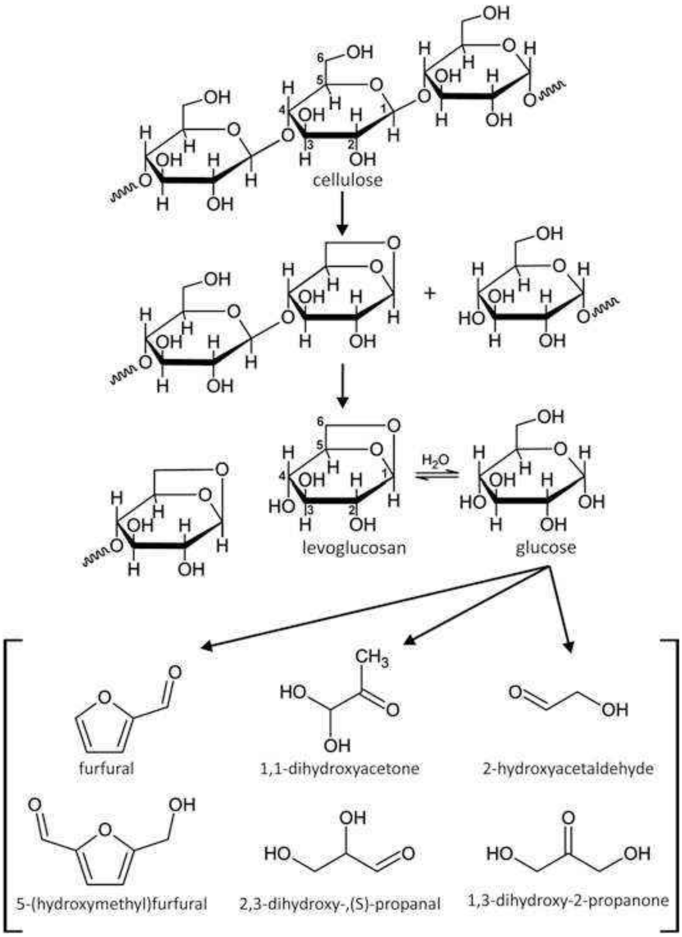


Fig. 3.1 Proposed pathway for the pyrolysis of cellulose

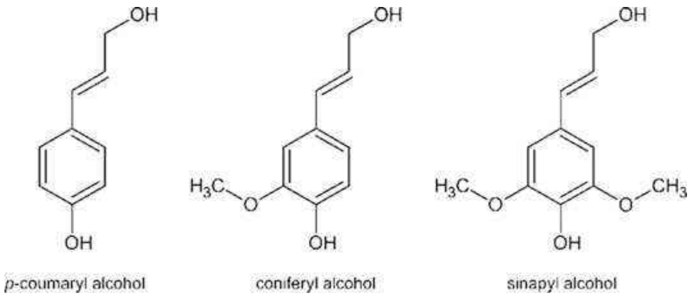


Fig. 3.2 Three main lignin precursors: *p*-coumaryl, coniferyl, and sinapyl alcohols (IUPAC names are 4-[(E)-3-hydroxyprop-1-enyl]phenol, 4-[(E)-3-hydroxyprop-1-enyl]-2-methoxyphenol, and 4-[(E)-3-hydroxyprop-1-enyl]-2,6-dimethoxyphenol, respectively)

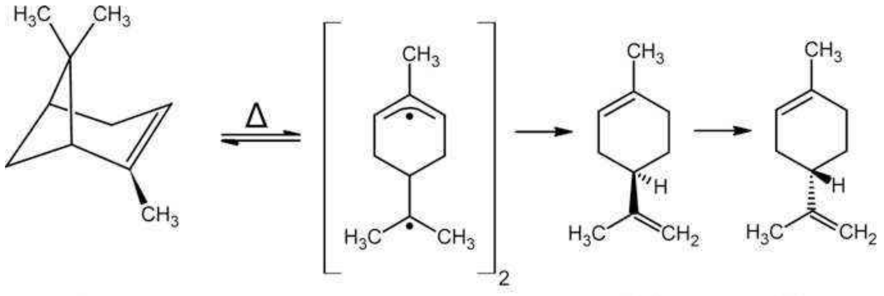
Repeated random chain scission followed by cyclization within the remaining cellulose oligomer will eventually "unzip" the molecule into the corresponding monomer. Levoglucosan then undergoes further reactions to produce a variety of other compounds [19].

Different mechanisms have been proposed in the literature for the formation of these other compounds, such as the furans (e.g., furfural, furfuryl alcohol, and 5-hydroxymethylfurfural [5-HMF]) [17–19]. For example, it has been proposed that, beginning with levoglucosan, the intermediate glucopyranose (glucose) may be formed via ring-opening between the oxygen and C1 of the C6–O–C1 cycle, followed by rehydration [19]. It is then proposed that the glucopyranose immediately undergoes a variety of secondary reactions to form other species such as furans, hydroxyacetaldehyde, aldehydes, and ketones, which are often present in fire debris samples [20].

Lignin is a cross-linked polymer, and it is commonly accepted that it is formed via an enzyme-mediated polymerization of three phenolic alcohols: *p*-coumaryl, coniferyl, and sinapyl [21] (Fig. 3.2). Thus, lignin is largely composed of phenylpropane units [22] which account for the abundance of substituted phenolic compounds generated when wood is pyrolyzed [13, 23]. The prominent molecular structures in softwood lignin have been proposed [24]. Pyrolysis of lignin primarily produces volatile monomeric compounds, including various alkylphenols and methoxy-substituted alkylphenols [23]; however, secondary reactions that recombine monomeric species into their respective dimers have been observed and serve to demonstrate the complexity and variety of reactions that may occur under pyrolytic conditions [23]. Some of the possible reaction pathways for the formation of lignin pyrolysis products have been summarized elsewhere [25–27].

Thermal Rearrangement

A special case of pyrolysis is the generation of new isomers by thermal rearrangement. A good example of thermal rearrangement is the conversion of α-pinene to



1 2 (+)-3 (-)-3

Fig. 3.3 Thermal conversion of α-pinene 1 via biradical 2 to produce racemic mixture of limonene 3 (dipentene)

limonene and other isomers [28] which are often detected in samples of fire debris containing softwood. The monoterpene α-pinene is often released via distillation when heat is applied to softwood lumber. While this thermal isomerization has been known for a long time [29], the mechanism and kinetics by which it occurs were not elucidated until more recently [30, 31]. In the gas phase, α-pinene converts to a resonance stabilized allyl-type biradical intermediate before undergoing a hydrogen shift from the isopropyl substituent to C1 to form a racemic mixture of limonene [31] (Fig. 3.3). A gas-phase kinetic study showed that the conversion of α-pinene to limonene increases with increasing temperature between 300 and 500 °C [31]. Thus, it is not unexpected to identify limonene in fire debris containing softwoods. It is important to note that limonene is also used as a fragrance in many consumer products, including household cleaners, and even in fire suppression foams, so it may be indigenous to the fire scene or added as a result of fire suppression activities.

3.2.2 Plastics

Synthetic polymers, known as plastics, have an important role in modern buildings and motor vehicles. In both building construction and interior design, plastics have replaced traditional building materials such as wood, glazed clay products, and nonferrous metals [32]. Plastics are usually less expensive than traditional building materials and often perform certain functions better. Plastics are used in furniture, flooring, plumbing, thermal insulation, decorative moldings, coatings, adhesives, fabrics, and upholstery foams. In the late 1980s, a series of review articles were published that examined the thermal decomposition products for seven different types of plastics commonly found in structures such as residences and offices [33–39]. Even though these review articles were published in the 1980s, many of these plastics are still used in our homes, offices, and vehicles and so their products of combustion are likely to be present in debris collected from a fire scene [40, 41].

In most fire debris samples submitted for analysis, it is expected that multiple sources of different types of plastics will contribute to the background of thermal decomposition products present in the fire debris. The thermal decomposition products common to more than one type of plastic, as compiled by Levin, are summarized in Table 3.1. In addition, it should be noted that at the time of the review article from which the data in Table 3.1 was published, polyurethane was more commonly used in rigid foam heat-insulating material in the building industry, while the past few decades have seen a rise in the use of flexible polyurethane foams—often treated with fire retardant—in furniture cushions and mattresses, carpet underlay, and consumer spray foam used for sealing cracks. From a pyrolysis point of view, it does not matter if the polyurethane is in the form of a rigid board or a flexible cushion; the degradation products from a fire will remain the same with the most common compound produced being the cyclic oxygenate 1,4-dioxane [42]. Finally, some of the compounds listed in Table 3.1, such as methyl ethyl ketone (2-butanone) and tetrahydrofuran (oxolane), may have come from residual solvent used in the manufacturing process. While these compounds may be reported by the fire debris examiner, it must be acknowledged that these compounds are not necessarily foreign to the scene because they are common solvents used in adhesives.

Absent from the list in Table 3.1 are the pyrolysis products from polypropylene, a common thermoplastic. The major product produced by polypropylene pyrolysis is 2,4-dimethyl-1-heptene, followed by a series of characteristic alkene doublets (C_{12} and C_{13}) and triplets (C_{15} and C_{16}) [43].

Degradation Pathways

It is helpful to understand that the compounds produced from burning plastic follow certain discrete degradation pathways. In general, three main pathways or mechanisms, by which thermal degradation products are formed from polymers, have been identified [44]:

- **Monomer reversion**;
- **Random chain scission**; and
- **Side group scission**.

Some polymers will thermally degrade mainly via a single mechanism, while others will not favor any one particular mechanism and will degrade via more than one mechanism. For example, the pyrolysis of poly(α-methyl styrene) will undergo monomer reversion almost exclusively to yield approximately 95% monomer, whereas oxidative pyrolysis of polystyrene will only produce approximately 27% monomer with the remaining products being a mixture of aromatic compounds [45], presumably generated via side group scission [44]. The degree to which a polymer will undergo monomer reversion is related to the chemistry of the side groups. When none of the side groups are hydrogen atoms, monomer reversion tends to be very high [46]; that is, the polymer will "unzip" and revert almost

Table 3.1 Thermal decomposition products common to more than one type of plastic typically found in structures [41]

Class	Compound	Number[a]	Class	Compound	Number[a]
Hydrocarbons	**Alkanes**		**Hydrocarbons—*continued***	**Aromatics—*continued***	
	Ethane	6		Propylbenzene	3
	Methane	5		Methylphenol	2
	Propane	5		Xylenes	2
	Butane	3		Ethyltoluene	2
	Hexane	3		Isopropylbenzene	2
	Pentane	3		α-Methylstyrene	2
	Cyclohexane	2		β-Methylstyrene	2
	Heptane	2	**Oxygenates**	**Alcohols**	
	Nonane	2			
	Octane	2		Phenol	5
	Trimethylcyclopentane	2		Ethanol	4
	Alkenes			Methanol	4
	Butadiene	6		**Aldehydes**	
	Ethylene	6		Acetaldehyde	5
	Propylene	6		Prop-2-enal	5
	Pentene	5		Benzaldehyde	4
	Butene	4		Formaldehyde	4
	Cyclohexene	4		Octanal	2
	Acetylene	3		Propanal	2
	Cyclopentene	3		**Ketones**	
	Hexene	3		2-Propanone	4
	Methylcyclopentene	3		1-Phenylethanone	3
	1,3-Pentadiene	2		2-Hexanone	2

(continued)

Table 3.1 (continued)

Class	Compound	Number[a]	Class	Compound	Number[a]
	1,4-Pentadiene	2		Cyclohexanone	2
	1,5-Hexadiene	2		Cyclopentanone	2
	2-Methyl-1-butene	2		2-Butanone (MEK)	2
	3-Methyl-1-butene	2		**Ether**	
	Cyclohexadiene	2		2-(2-methoxypropoxy)-propan-1-ol	2
	Cyclopentadiene	2		**Carboxylic acids**	
	Heptene	2		Acetic acid	3
	Hexadiene	2		Benzoic acid	2
	Isobutene	2		Formic acid	2
	Methylcyclohexene	2	**Other**	**Halogenated**	
	Pentadiene	2			
	Propadiene	2		Chlorobenzene	2
	Propene	2		Chloroethane	2
	Propadiene	2		Chloroethylene	2
	Aromatics			Chloromethane	2
	Benzene	6		Dichlorobenzene	2
	Styrene	6		**Heterocyclics**	
	Toluene	6		1,2-Oxazole	2
	Ethylbenzene	5		Pyridine	2
	Naphthalene	3		Oxolane (THF)	2

[a] Number refers to the number of different plastics which observed to give off the listed compound during pyrolysis. A total of seven plastics were examined: acrylonitrile–butadiene–styrene (ABS), nylon, polyester, polyethylene, polystyrene, poly(vinyl chloride), and rigid polyurethane foam

entirely back to the monomer constituents from which it was originally formed. If at least one of the side groups is a hydrogen atom—an α-hydrogen—then random chain scission and even side group scission are likely to play a more significant role. The reason for this is that the presence of an α-hydrogen allows decomposition via a free radical chain reaction. The reaction proceeds via the thermal breaking of a C–C bond in the polymer backbone to form either two long-chain free radicals via random chain scission, or one free radical chain and one monomeric free radical via end chain scission [47]. An α-hydrogen and the free radical can exchange positions within the same polymer chain (*intra*molecular transfer) or between chains (*inter*molecular transfer), and scission at the new radical center may then result in further fragmentation of the polymer chain (see Fig. 3.4). When the α-hydrogens are replaced by a different functional group, such as a methyl or phenyl, random chain scission is less favored and monomer reversion will tend to dominate the thermal degradation reaction [46].

Thus, in the case of polyethylene [R_1=R_2=H], polypropylene [R_1=H, R_2=CH_3], and poly(methyl acrylate) [R_1=H, R_2=$COOCH_3$], the *presence* of α-hydrogens is correlated with low monomer reversion and higher random chain scission, while the *absence* of α-hydrogens is correlated with higher monomer reversion and less random chain scission as seen in the thermal degradation of poly(methyl methacrylate) [R_1=CH_3, R_2=$COOCH_3$] and poly(α-methylstyrene) [R_1=CH_3, R_2=C_6H_5]. There are exceptions, such as polystyrene [R_1=H, R_2=C_6H_5], which has α-hydrogens but does not undergo as much chain scission as might be expected. In simple terms, the phenyl moiety in polystyrene may help to stabilize the free radical, thus making the free radical less reactive and allowing more monomer reversion and side group reactions to occur.

Polyethylene is an important polymer to consider in terms of thermal degradation and the resulting interfering compounds that may be present in fire debris. Polyethylene is a common thermoplastic used to manufacture many different types of materials, including containers such as plastic gasoline cans (jerrycans) that may be present at a fire scene. Polyethylene will undergo random chain scission almost exclusively during pyrolysis to generate a homologous series of triplets typically over the carbon range C_8–C_{20} and higher. Each triplet is comprised of the diene, alkene, and alkane having the same number of carbon atoms, with the alkene being the dominant product in each triplet [48, 49] (see Fig. 3.5).

Pathways based on scission of the C–C bond, with concomitant hydrogen abstraction and radical formation, have been proposed to explain the production of short-chain alkene and alkane products, but a secondary dehydrogenation pathway to produce the diene remains elusive [50]. The ratios of saturated to unsaturated hydrocarbon within each triplet will vary with pyrolysis temperature [48–50]. The homologous series of short-chain hydrocarbons produced by the pyrolysis of polyethylene can not only mimic a petroleum distillate but, when in high concentration, can easily mask the peaks from an ignitable liquid in a chromatogram. Recognition of the diagnostic triplet pattern produced by thermal degradation of polyethylene will prevent misidentification of these degradation products as a petroleum distillate. The use of extracted ion profiles will assist in confirming the

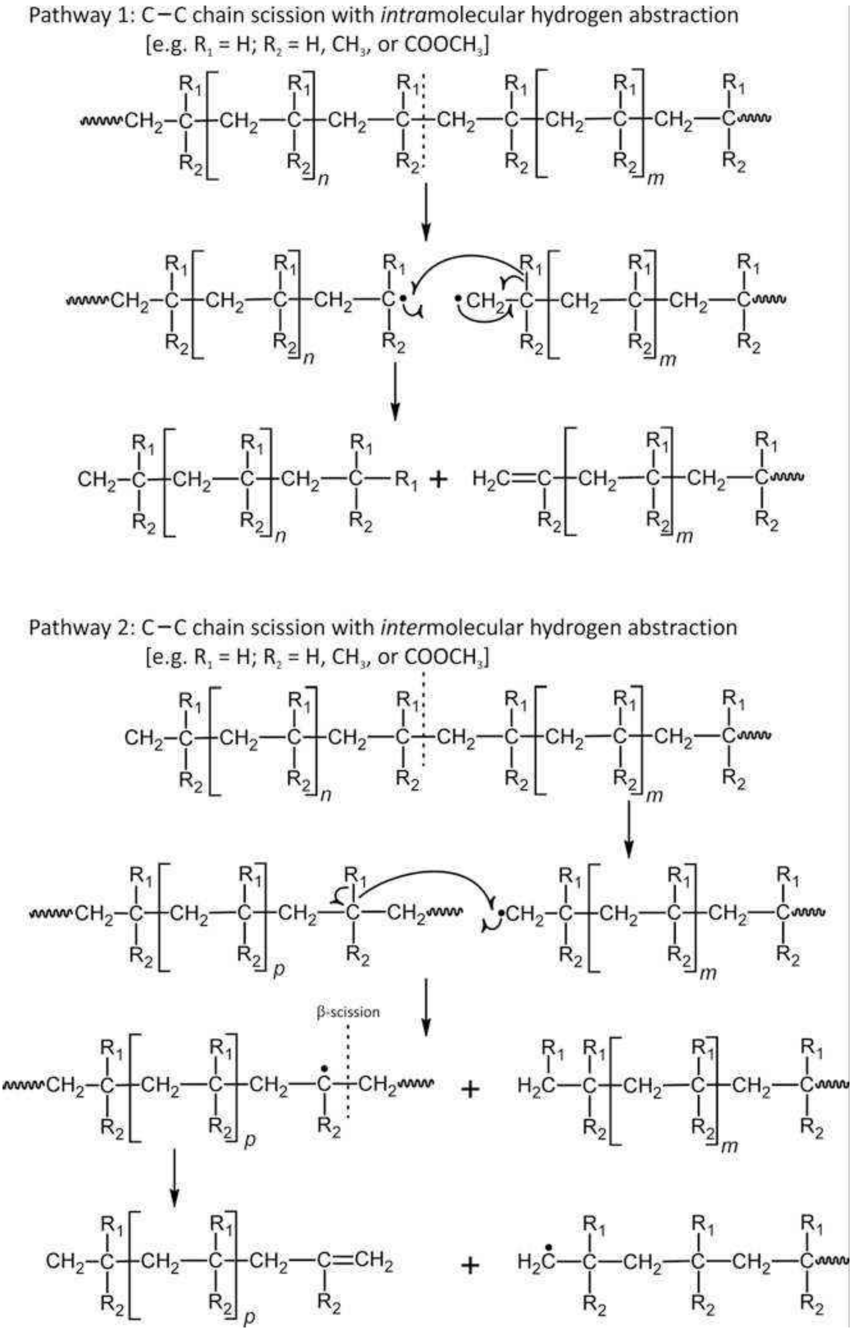

Pathway 1: C−C chain scission with *intra*molecular hydrogen abstraction
[e.g. R_1 = H; R_2 = H, CH_3, or $COOCH_3$]
Pathway 2: C−C chain scission with *inter*molecular hydrogen abstraction
[e.g. R_1 = H; R_2 = H, CH_3, or $COOCH_3$]
β-scission
R_1
R_2
CH_2
H_2C
n
m
p

Fig. 3.4 Proposed reaction pathways for polymer random chain scission

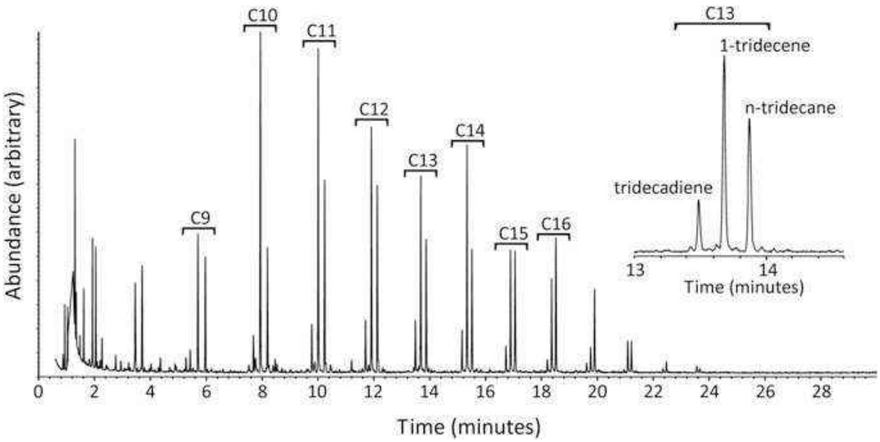


Fig. 3.5 GC-MS total ion chromatogram (TIC) of thermal degradation products from a polyethylene shopping bag burned with an open flame in the author's laboratory

presence of an underlying ignitable liquid if the total ion chromatogram is dominated (masked) by the degradation products of polyethylene [51].

Side group scission occurs when the molecular bonds between substituents and the polymer chain are weaker than the bonds in the polymer backbone resulting in all or part of the group attached to the polymer backbone preferentially splitting off [52, 53]. Side group scission is common during pyrolysis and may take place before random scission of the chain [47]. The pyrolysis mechanism of poly(vinyl chloride) (PVC) provides a good example of side group scission which results in the elimination of hydrochloric acid (HCl) and the formation of a conjugated polymer backbone (a polyene). Chain scission of the polyene will produce conjugated fragments of varying lengths which may then undergo intramolecular cyclization to produce benzene as well as other aromatic compounds such as toluene, styrene, biphenyl, indene, naphthalene, and 1-methylnaphthalene [54–57]. Montaudo and Puglisi have proposed two separate pathways, one involving *intra*molecular cyclization to form unsubstituted aromatics and another involving *inter*molecular cross-linking followed by cyclization to form alkyl-substituted aromatics [57] (see Fig. 3.6).

Moldoveanu gives a more comprehensive list of the alkylaromatic compounds, including ethylbenzene and the xylenes, formed during the pyrolysis of PVC in an inert atmosphere [47]. While some of these alkylaromatic compounds will be the same as those present in several classes of ignitable liquids (e.g., gasoline), their mere presence in the absence of an ignitable liquid should not lead to the conclusion that an ignitable liquid is present. The identification of an ignitable liquid is based on the observation of extracted ion profiles (EIPs) which, when compared to EIPs of known ignitable liquids, must have the expected compounds in the correct relative ratios. Occasionally, the presence of high concentrations of alkylaromatic compounds from thermal degradation will distort the diagnostic pattern for an

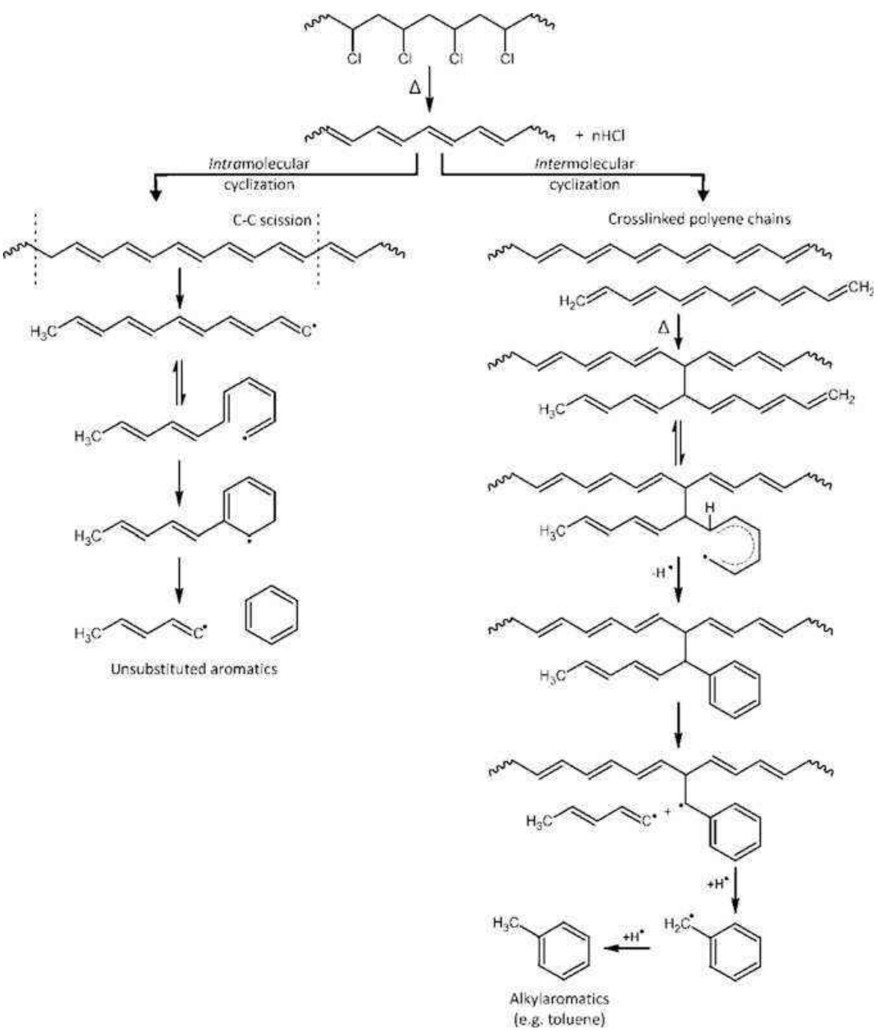

Cl
Cl
Cl
Cl
Δ
+ nHCl
*Intra*molecular cyclization
*Inter*molecular cyclization
C-C scission
Crosslinked polyene chains
H3C
C•
CH2
H2C
Δ
H
-H•
+
+H•
Unsubstituted aromatics
Alkylaromatics (e.g. toluene)

Fig. 3.6 Proposed reaction pathways for poly(vinyl chloride) side group scission (adapted from [57])

ignitable liquid so much that an identification of an underlying ignitable liquid cannot be made.

Carpet

The volatiles generated when carpet burns in a fire are a special case of burning plastics and have received additional attention in the scientific literature. Carpet and rugs are used extensively in residences, offices, and motor vehicles, and have been reported to be the most commonly encountered material submitted by fire investigators [58–60]. Carpet, and other flooring materials, are often collected from fire scenes because it is often more protected from the heat of the fire by virtue of it being the lowest part of the room, as well as being protected by furniture and materials dropping down from the burning ceiling. The potential of volatiles from carpet to interfere with the identification of an ignitable liquid was first assessed by Howard and McKague [61], who identified the hydrocarbons benzene, toluene, and styrene in charred carpet. Their findings were corroborated by a later study that compared the volatiles from burned and unburned samples of carpet [5]. In another study, Bertsch noted the presence of ethylbenzene, xylene isomers, styrene, naphthalene, and methylnaphthalenes arising from the combustion of carpet [62]. In addition to these compounds, Keto noted the presence of many compounds common to gasoline in a carpet pyrolysate, including indane, methylindanes, and various branched cyclohexanes [63]; however, the relative ratios of these compounds were found to be inconsistent with gasoline. New, unused motor vehicle mats were tested for background volatiles and the most common compounds found in these mats were all three xylene isomers and limonene (dipentene) [64]. In the study of motor vehicle mats, the authors suggested that limonene likely came from a solution used to clean the carpet.

3.2.3 Human Combustion Products

Inevitably, some fires will involve a body, the burning of which may contribute to the background of interfering products present in samples collected from the scene. In some cases, the presence of the body is accidental; the person died unintentionally and was a victim of an accidental fire. In other cases, the fire was set in an attempt to kill the occupants of a residence or to conceal a crime such as homicide [65–67]. Two recent studies from Australia have concluded that arson-associated homicides are on the rise, and one of the key reasons behind this increase is the ability of fire to destroy DNA, fingerprints, and other evidence, thus hampering homicide investigations [68, 69].

In situations where fire is used to conceal a homicide, it is not uncommon for an ignitable liquid to be poured over the body and a fire set. Thus, materials collected from a fire scene involving a body may include samples of clothing or hair from the deceased, or samples from underneath the body (carpet/underlay, bedding/mattress, or, if the body was burned outside, soil) where the ignitable liquid may have been wicked, and had not been burned off. The combustion of body tissue is often limited to the near-surface which is predominantly subcutaneous fat [70]. Pyrolysis products from the burning of a body may condense on materials near to or in contact with the body, and will thus be part of the volatile matrix of any samples collected for analysis. The main pyrolysis products from fat are a homologous series of n-alkanes (C_9–C_{13}), n-alkenes (C_7–C_{13}), and n-aldehydes (C_5–C_{10}), plus some dienes (C_{10}–C_{12}) [71]. While no significant differences were observed in the products generated from the fat of different species (human, pig, chicken) [71], it has been observed that the presence of a homologous series of n-aldehydes (C_5–C_9) is a good indicator of the presence of burned human or animal remains [72]. However, it should be noted that the pyrolysis products observed are dependent on temperature, and very high temperatures (i.e., >700 °C) will cause additional cracking and oxidation of the initial pyrolysis products which will result in fewer straight-chain aldehydes [71].

3.3 Interference from Unburned Materials at the Fire Scene

Samples of burned substrates are not the only materials that may be collected from a fire scene to determine if an ignitable liquid may be present. Unburned materials may also be submitted for analysis for a variety of reasons, including failure of the ignitable liquid poured by the arsonist to ignite. In situations such as these, the arsonist may have poured an ignitable liquid in multiple locations throughout a structure, but only ignited the pour closest to the exit; the resulting fire may not transmit to the remaining unburned pours which, when discovered by the investigator, will be submitted for analysis. Alternatively, a fire may cause collapse of a ceiling or furniture, which can fall down onto unburned or partially burned areas. The collapse effectively protects these areas from the fire and prevents the burning off of ignitable liquids present in that area as well.

3.3.1 Household and Building Materials

The use of a large number of synthetic materials in residential and commercial buildings has spawned an interest by scientists to measure the volatile organic compounds emitted by those materials and has led to the development of a material emission database for materials common to North America [73]. For example, the material emission database lists the four or five most abundant volatile organic compounds released by several unburned carpets, and the results are reproduced in Table 3.2. Fernandes et al. reported traces of carbon disulfide, ethyl acetate, benzene, and toluene in an unburned doormat from Hong Kong [5]. They suggested that the small amount of carbon disulfide detected came from the rubber padding on the back of the carpet.

In the case of other materials encountered at a fire scene, residual solvents (i.e., ignitable liquids) may be present as part of the manufacturing process and subsequently detected during routine fire debris analysis. For example, residual solvent used in the manufacture of vinyl sheet flooring has been reported [74]. In this study, some samples of vinyl flooring were found to contain either an isoparaffinic (i.e., Isopar H®) or a normal alkane (i.e., Norpar®) product.

Table 3.2 Volatile organic compounds (VOCs) emitted by residential and commercial carpet [73]

Residential		Commercial	
Sample	VOC	Sample	VOC
Nylon carpet, latex backing	Heptane *p*-Xylene Undecane 4-Phenylcyclohexane Cyclodecane	Olefin carpet, latex backing	2,2,4-Trimethylpentane Dodecane Tridecane 4-Phenylcyclohexane Cyclodecane
Nylon carpet, latex backing	*Styrene* *Dodecane* *4-Phenylcyclohexane* *Cyclodecane*	*Polypropylene carpet, latex backing*	*2,2,4-Trimethylpentane* *Styrene* *Tridecane* *4-Phenylcyclohexane*
Nylon carpet, latex backing	Styrene Dodecane Tridecane 4-Phenylcyclohexane Tetradecane	Nylon carpet, backing not specified	2,2,4-Trimethylpentane Styrene Undecane Tridecane 4-Phenylcyclohexane

Aftermarket products applied by consumers may also result in residual solvent being present at a fire scene. As an example, the application of an exterior waterproofing product, or “sealer,” to concrete or wood will result in detectable amounts of carrier solvent—in this case a medium petroleum distillate—for nearly one month after application [75]. Solvents used in coatings designed for interior application, such as wood floor stain or polyurethane sealer, may persist for much longer periods of time. Lentini made separate applications of wood stain, wood stain topped with polyurethane wood floor sealer, and a drying oil to unfinished pine and oak floorboards, and tested them for residual solvent over a period of 24 months [76]. This study showed that all floorboards contained residual solvent two years after application of the finishing product. Note that the exterior sealers were exposed to direct sunlight throughout the study, which may account for the more rapid loss of solvent compared with the interior coatings.

The presence of various volatile organic compounds (VOCs) has been reported in not only unburned building materials [73], but also those arising from unburned household products such as newspapers and plastic utensils [77], and even toys [78]. Some of the volatile organic compounds present in the indoor environment are the products of microbial metabolism (mold and fungi), the most common of which are alcohols (e.g., isomers of methylbutanol and octenol), furans (e.g., 3-methylfuran), and ketones (e.g., 2-hexanone) [79]. Many of the materials reported in the literature typically do not contain a series of compounds that, under careful scrutiny, would be mistaken for an ignitable liquid. However, as shown in the above examples such as vinyl sheet flooring, there are materials that are known to contain solvents that will be accurately identified as an ignitable liquid [80]. Other materials that are known to contain an ignitable liquid include paper products such as cardboard, adhesives used on paper products or in construction (e.g., “liquid nails” used to hold sheets of drywall to wood studs), flooring [80], and pieces of asphalt shingle [81]. Other common household products, such as some insecticides, containers of enamel paint or varnish, and correction fluids, contain solvent that may become involved in the fire and therefore be present in the fire debris that is collected.

It is important that the forensic scientist knows which materials may contain residual solvent and understands that, under a given set of circumstances, an ignitable liquid may not be foreign to the fire scene. Note that ignitable liquids identified in a sample of fire debris are not called “accelerants” because the examiner has no way of knowing if the ignitable liquid is indigenous or foreign to the scene. As mentioned earlier, the mere presence of an ignitable liquid in fire debris does not mean an ignitable liquid was brought to the scene by an arsonist to accelerate the fire. The fire investigator will take into account many other factors at a fire scene, including other possible ignition sources and where the fire started, before deciding if an arson occurred. For example, finding gasoline in the debris from a garage fire where a gasoline-powered lawn mower was stored may mean that arson was not the cause of the fire; however, finding gasoline on the charred remains of a bed where a murder victim lay may be indicative of arson.

3.3.2 Interference from Clothing

Clothing may be used to start a fire, with or without the addition of an ignitable liquid, or clothing may be seized from an individual suspected of starting a fire with an ignitable liquid. A recent study found that when two liters of gasoline were poured onto a floor, a significant amount of gasoline was recovered from the footwear and clothing of the person involved in the activity [82]. For this reason, investigators may seize clothing from a suspect to be analyzed for ignitable liquids. In either situation, it is important for the forensic scientist to know what naturally occurring compounds are common to clothing and are to be expected in the background.

Residual Solvents in Footwear and Clothing

While not necessarily collected from a fire scene, clothing from a fire or from a suspected arsonist is a special case where volatiles may be present on materials associated with the scene. Clothing may contain residual solvents from the manufacturing process. T-shirts which have a vinyl decal applied to their surface may contain a residual amount of solvent such as toluene [80]. Studies on clothing have also found that some cotton garments (e.g., pajamas and denim fabrics) and synthetic garments (e.g., spandex shorts) may contain traces of petroleum distillates [80]. Shoes are particularly problematic for investigators, as volatile solvents are used during the construction of shoes. The adhesives used to bond footwear uppers to their soles are known to contain volatile solvents such as toluene [83], and other solvents such as methyl ethyl ketone, 3-methylpentane, and 2-methylpentane have been reported in some shoe factory glues [84]. Other compounds such as acetone, heptane, and n-hexane [85] have also been identified as common solvents related to gluing activities in footwear manufacturing. The molded synthetic material used in footwear construction, primarily poly(vinyl chloride) and polyurethane [85], may also contain a variety of aromatic hydrocarbons and petroleum distillates [86].

Human Skin Volatiles

Volatile compounds may be excreted through the skin of the wearer and absorbed by the clothing fabric, or microbial action occurring on the individual's skin may generate volatile compounds that are then absorbed and retained by the clothing.

Acetone is a compound that is known to be excreted through the skin, and is often associated with physical activity. For example, an individual apprehended by a peace officer may have fled the scene or have perspired as a result of a physiologic response to the circumstances surrounding the setting of the fire. In these situations, it is common to detect elevated levels of acetone in the individual's clothing [87]. While a diverse range of ketones, aldehydes, carboxylic acids, alcohols, and even alkanes may be either excreted through the skin or produced by microbial flora living on the skin (e.g., in the axillary region), the four compounds most commonly reported in the scientific literature are the two aldehydes decanal and nonanal, and the two ketones 6-methyl-5-hepten-2-one and (E)-6,10-dimethyl-5,9-undecadien-2-one (geranylacetone) [88]. The 20 compounds most frequently isolated from human skin are listed in Table 3.3, with six of the top ten being aldehydes.

A study of volatiles from human hands demonstrated that different textiles preferentially absorb different volatiles [89]. Thus, while cellulosic fabrics such as cotton and rayon absorbed a wide range of compounds having different functional groups, polyester textiles tended to isolate acidic volatile compounds not normally seen on other types of fabrics. Clothing seized from a suspect may contain more than just the by-products of normal human sweat. It has been known for decades

Table 3.3 Twenty compounds most frequently isolated from human skin [88]

Compound		Compound	
1	Decanal	11	Hexadecane
2	Nonanal	12	Methyl hexanoate
3	6-Methyl-5-hepten-2-one	13	Pentadecane
4	Geranylacetone	14	Undecane
5	(*E*)-2-Nonenal	15	(*E*)-3-Methyl-2-hexenoic acid
6	Undecanal	16	(±)-limonene
7	Hexanal	17	Methyl dodecanoate
8	Octanal	18	Indole
9	Acetic acid	19	Methyl hexadecanoate
10	Benzyl alcohol	20	Propanoic acid

that a measurable amount of ingested alcohol is excreted through human skin [90] and so it is possible to detect ethanol absorbed by clothing worn by a suspect who had recently ingested alcohol. Thus, the presence of alcohol on a suspect's clothing does not necessarily mean that the suspect used alcohol to accelerate the fire.

On a related note, background volatiles excreted from human skin are also expected to be present on samples taken from the hands of a suspect. The testing of a person's hands will commonly yield the following six background volatiles: 2-furancarboxaldehyde, 2-furanmethanol, phenol, nonanal, decanal, and dimethyl hexanedioate [88]. Foreign volatiles may also be isolated from human skin; for example, it is also possible to find gasoline—or any other ignitable liquid poured at the scene—on the hands of a suspect [91].

3.3.3 Interference from Decomposing Human Remains

As previously discussed in Sect. 3.2.3, a burned body will contribute interfering compounds; the continuing decomposition of a human body can also contribute interfering products. Remote fire scenes involving an unburned or partially burned body, such as a secluded residence where the fire remained undetected for a significant length of time, or the body of a murder victim that was dumped in a remote area and partially burned, may contribute volatile compounds to the fire debris sample. The volatiles produced from the decomposition of unburned human tissue have been the subject of several studies related to the detection of buried human remains in homicide investigations and the recovery of victims of mass disaster. Intestinal microbiota and communities of microorganisms in the outer environment are responsible for the decomposition of human remains. The microorganisms in the outer envirfonment will differ depending on the geographic location, and the volatiles produced will vary somewhat with the specific habitat (e.g., forest, cultivated field, and urban) [92]. A number of compounds evolved during decomposition are commonly observed regardless of the location of the body; these are listed in Table 3.4. It is important to note that none of these peaks would generally be identified as an ignitable liquid.

When isolated from the local external environment, the early stages of human decomposition will give rise to the following eleven compounds over a 24-h period: oxygenates (ethanol, 2-propanone, and 2-butanone), dialkyl polysulfides (dimethyl disulfide, methyl ethyl disulfide, and dimethyl trisulfide), and hydrocarbons (toluene, octane, *o*-xylene, *m*-xylene, and *p*-xylene) [93]. While some of these individual compounds may also be present in certain solvents (e.g., ethanol or 2-propanone), the examiner should acknowledge other possible sources in the report. Other compounds, such as the aromatic hydrocarbons, will not be present in the same ratios found in certain ignitable liquids and so should not be identified as an ignitable liquid.

Table 3.4 Common decomposition products observed from different locations: forest, cultivated field, and urban [92]

Acids	**Nitrogen compounds**
Propanoic acid	Acetamide
Butanoic acid	*N*-Methylacetamide
2-Methylpropanoic acid	*N*,*N*-Dimethylformamide
2-Methylbutanoic acid	*N*,*N*–Dimethylacetamide
3-Methylbutanoic acid	*N*,*N*–Dimethylnitrous amide
Pentanoic acid	Trimethylamine
Hexanoic acid	**Sulfur compounds**
Esters	Methanethiol
Butyl formate	Methyldisulfanylmethane
Butyl butanoate	Methylsulfanyldisulfanylmethane
Butyl 3-methylbutanoate	**Cyclic hydrocarbons**
2-Methylester, propanoic acid	Cyclohexylcyclohexane
Ketones	Phenol
2-Pentanone	4-Methylphenol
Aldehydes	Piperidin-2-one
Butanal	Quinazoline
Alcohols	**Non-cyclic hydrocarbons**
2-Methyl-1-propan-1-ol	Eicosane
1-Butanol	2-Methylprop-1-ene
(2*S*)-Butanol	
3-Methylbutan-1-ol	
1-Pentanol	

3.4 Interference from Fire Suppression and Fire Investigation

3.4.1 *Fire Suppression Foams*

Fire suppression activities and the subsequent investigation of the origin and cause of the fire after it is extinguished may impart interfering compounds into the fire debris sample sent to the laboratory for analysis. Fires are generally classified as either Class A or Class B. Class A fires involve a structure or wildland fire, and a Class B fire is a flammable liquid spill or a tank fire. Due to the high surface tension of water, much of what is applied to a Class A fire will run off the surface onto which it is sprayed, reducing its effectiveness [94]. To combat this phenomenon, a fire suppression foam may be used. In general, a Class A fire suppression foam contains a surfactant and a foaming agent, which are mixed with water at the fire scene. The surfactant will decrease the surface tension of the water, which will allow the water to better flow over and penetrate the material that is burning instead of ricocheting off, which will also more effectively cool the fire. The foaming agent will form an air-excluding barrier, which will smother the fire. A Class B fire suppression foam is formulated to produce a thin foam layer when sprayed on the surface of a flammable liquid. This foam layer will reduce heat transfer from the fire to the surface of the fuel, thus reducing the conversion of the liquid fuel to the vapor phase and thereby starving the fire of additional fuel [95].

The use of Class A fire suppression foams on a structure fire may leave a residue of surfactant and/or foaming agent on the fire debris. In one study, five Class A fire suppression foams were sampled by heated headspace extraction and analyzed by gas chromatography using flame ionization detection [96]. While peaks in the C_8–C_{16} range were detected in some of the foams, the authors concluded that none of the patterns could be mistaken for a petroleum distillate. Another study of Class A foams concluded that while limonene, a component of the foam, was present in all tests, the foam contributed no significant interference that would hamper interpretation of the analytical results [97]. Pyrolysis of sodium dodecylbenzenesulfonate, a surfactant that may be present in some fire suppression foams, has been shown to produce a series of C_{11}- through C_{13}-alkylbenzene compounds (e.g., (1-butylheptyl) benzene, (1-pentylheptyl) benzene, and (1-ethyldecyl) benzene) [98]. Other aromatic compounds, such as toluene, ethylbenzene, the xylenes, propylbenzene, 1-ethyl-2-methylbenzene, indane, naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene, were also formed during the pyrolysis of this surfactant, demonstrating that, depending on the formulation, the use of fire suppression foam may give rise to interfering compounds in a sample of fire debris. These compounds will not occur in a pattern that would be confused with those observed in ignitable liquids that contain these compounds.

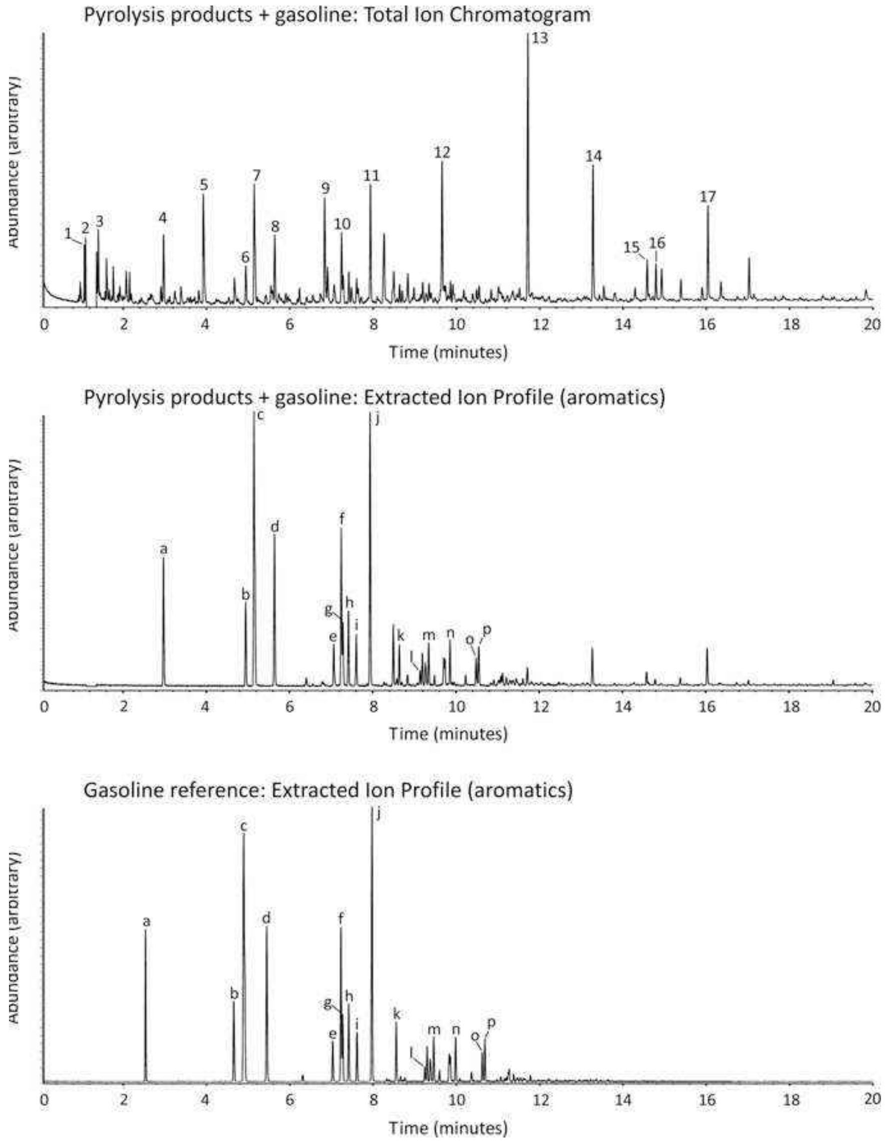
3.4.2 Collection Materials

Fire investigators are most likely to use disposable gloves to collect samples at a fire scene [99], and some may place their gloves in the container with the fire debris. The practice of including the gloves with the sample is meant to demonstrate that a new pair of gloves was used to collect each sample, ostensibly, to prevent secondary transfer of volatiles via the gloves from one sample to the next; however, no studies have been conducted to demonstrate that this may even be possible. The addition of a pair of disposable gloves to a sample of fire debris may be a source of interfering compounds arising either from the manufacturing processes used to make the gloves (including mold release agents) and/or from contamination of the gloves during storage and transport to the scene. A variety of different types of gloves, including fabric, leather, and two types of disposable gloves—latex and nitrile—were tested for background volatiles [100]. Some types of disposable gloves were found to have a high background of interfering compounds. For example, cycloalkanes in the range of C_{10} to C_{12} were detected in one type of nitrile glove [100]. If the fire investigator wishes to submit the gloves used for collecting a sample, then the gloves should be packaged separately from the fire debris and submitted as an additional sample.

Investigators commonly use cellulose-based absorbent materials such as "cotton" balls, cotton gauze, and tampons to collect liquids at a fire scene when a vial is unavailable or when the liquid is not easily collected, such as a sheen on the surface of a puddle. The absorbed liquid is then sent to the forensic laboratory for testing to determine whether or not an ignitable liquid is present. Even though many of the above absorbents are sterile (i.e., free of pathogens), this is not the same as being free of volatile compounds, and experience has shown that these absorbents often contain interfering volatile compounds to varying degrees. To date, a comprehensive study of the background volatiles emitted by these different materials has not been conducted. Nevertheless, when an investigator submits a sample collected on an absorbent, it is a good practice for the forensic laboratory to request that a sample of new, unused absorbent—packaged in the same manner as the absorbed sample—be submitted separately so that it may be tested for the presence of interfering compounds. In addition to cellulose-based absorbents, a variety of materials have been tested for their efficacy in absorbing ignitable liquids from concrete floors [101]. Unscented, non-clumping cat litter was found to be an effective absorptive media that will give rise to a negligible background [101].

3.5 Simulating Background Interference Compounds in the Laboratory

When interpreting chromatographic data obtained from fire debris, it is important that examiners take into account the substrates present when interpreting the data. There are numerous resources available that discuss the different interfering products, including an online database of burned and unburned substrates (see National Centre for Forensic Science Substrate Database [http://ilrc.ucf.edu/substrate/]). It is also important for forensic examiners to create comparison samples of pyrolysis products to use in the interpretation of chromatographic data obtained from fire debris. By generating pyrolysis data from many different substrates, a database or library cataloguing common pyrolysis compounds and their elution patterns may be created. The pyrolysis information will be invaluable for clearly identifying which compounds extracted from a sample of fire debris originated from the substrate and which came from an ignitable liquid. Over the years, various studies have attempted to simulate the production of these interfering products [61, 102]. For example, DeHaan and Bonarius burned samples of carpet and other floor coverings in a simulated structure fire and recovered the volatiles that came from the different substrates [7]. They found that carpet and carpet pad (underlay) produced a complex mixture of volatiles in the "middle petroleum distillate" range (C_8–C_{13}), but concluded that the products could be distinguished from common ignitable liquids such as gasoline. Other researchers have simulated the thermal decomposition of


Pyrolysis products + gasoline: Total Ion Chromatogram

Pyrolysis products + gasoline: Extracted Ion Profile (aromatics)

Gasoline reference: Extracted Ion Profile (aromatics)

Fig. 3.7 Simulated chromatogram showing compounds generated from the pyrolysis of kraft paper and spruce softwood (cellulose and lignin) which mask the gasoline profile. The presence of gasoline is shown in the extracted aromatic ion profile. Pyrolysis products were generated by heating for 20 min at 360 °C using a tube furnace [104]. Compound assignments are found in Table 3.5

various building materials by heating them with an open flame in clean, unused metal cans [62, 103], or by simply burning the material with a Bunsen burner and, once cooled, sealing the charred debris in a nylon bag [5]. A significant drawback to heating substrates with an open flame is that the conditions cannot be reproduced from one experiment to another because it is not possible to measure the exact temperature reached and the time the material is exposed to that temperature. More recently, an electric tube furnace was employed to reproducibly simulate the interfering compounds produced during a fire [104].

Figure 3.7 shows an example of a typical GC-MS total ion chromatogram (TIC) of the pyrolysis products from kraft paper (cellulose) and spruce (cellulose and lignin) heated at 360 °C for 20 min in a tube furnace [104]. This sample was then spiked with a small amount of 75% evaporated gasoline prior to GC-MS analysis. Visual inspection of the TIC shows that there is no discernable pattern of an ignitable liquid in the chromatogram; yet when extracting ion profiles of key compounds associated with ignitable liquids, such as the aromatics, the pattern for gasoline becomes clear (Table 3.5).

Table 3.5 Compounds identified in Fig. 3.7. Identification of pyrolysis compounds based on MS library search, and gasoline compound identifications based on published data[a]

Pyrolysis products + gasoline TIC			
1	Propan-2-one	10	1-Ethyl-3-methylbenzene
2	Furan	11	1,2,4-Trimethylbenzene
3	2-Methylfuran	12	2-Methoxyphenol
4	Toluene	13	2-Methoxy-4-methylphenol
5	Furfural	14	4-Ethyl-2-methoxyphenol
6	Ethylbenzene	15	2-Methoxy-4-(2-propenyl)phenol
7	*o*-Xylene	16	2-Methoxy-4-propylphenol
8	*p*- + *m*-xylene	17	2-Methoxy-4-(1-propenyl)phenol
9	5-Methylfurfural		
Pyrolysis products + gasoline: aromatic EIP (m/z^+ 91, 92, 105, 106, 119, 120, 134)			
a	Toluene	i	1-Methyl-2-ethylbenzene
b	Ethylbenzene	j	1,2,4-Trimethylbenzene
c	*o*-Xylene	k	1,2,3-Trimethyl benzene
d	*p*- + *m*-xylene	l	1,3-Diethylbenzene
e	Propylbenzene	m	1,4-Diethylbenzene
f	1-Methyl-3-ethylbenzene	n	1,3-Dimethyl-2-ethylbenzene
g	1-Methyl-4-ethylbenzene	o	1,2,4,5-Tetramethylbenzene
h	1,3,5-Trimethylbenzene	p	1,2,3,5-Tetramethylbenzene

[a] Johansen et al. [106]

3.6 Questions

1. Name the three different mechanisms by which background or potentially interfering compounds in fire debris samples may arise. Briefly describe each.
2. Name the three main pathways, or mechanisms, by which pyrolysis products are formed from polymers.
3. Using polyethylene as an example, describe why it is important to know what compounds are formed when polyethylene is burned in a fire.
4. What tissue in the human body is most likely to be consumed during a fire?
5. Name the compound classes of the interfering products normally produced from the burning of a body.
6. Why is it important to be aware of the types of volatile and semi-volatile compounds present in unburned substrates (building materials, furniture, clothing, etc)?
7. Give two examples of unburned materials that may contain residual solvent that is not foreign to the material.

References

1. ASTM E1412-16 (2016) Standard practice for separation of ignitable liquid residues from fire debris samples by passive headspace concentration with activated charcoal. ASTM International, West Conshohocken, PA, www.astm.org
2. ASTM E1413-13 (2013) Standard practice for separation and concentration of ignitable liquid residues from fire debris samples by dynamic headspace concentration. ASTM International, West Conshohocken, PA, www.astm.org
3. ASTM E1386-15 (2015) Standard practice for separation of ignitable liquid residues from fire debris samples by solvent extraction. ASTM International, West Conshohocken, PA, www.astm.org
4. ASTM E1618-14 (2014) Standard test method for ignitable liquid residues in extracts from fire debris samples by gas chromatography-mass spectrometry. ASTM International, West Conshohocken, PA, 2014, www.astm.org
5. Fernandes MS, Lau CM, Wong WC (2002) The effect of volatile residues in burnt household items on the detection of fire accelerants. Sci Justice 42(1):7–15
6. Baerncopf J, Hutches K (2014) A review of modern challenges in fire debris analysis. Forensic Sci Int 244(1):e12–e20
7. DeHaan JD, Bonarius K (1988) Pyrolysis products of structure fires. J Forensic Sci Soc 28 (5–6):299–309
8. International Union of Pure Applied Chemistry (1993) Nomenclature and terminology for analytical pyrolysis. Pure Appl Chem 65:2405–2409
9. Boettner EA, Ball GL, Weiss B (1973) Combustion products from the incineration of plastics. US Environmental Protection Agency, Cincinnati
10. Edye LA, Richards GN (1991) Analysis of condensates from wood smoke: components derived from polysaccharides and lignins. Environ Sci Technol 25(6):1133–1137
11. Trimpe MA (1991) Turpentine in arson analysis. J of Forensic Sci 36(4):1059–1073

12. Miller RB (1999) Structure of wood. In: Wood handbook—wood as an engineering material. Forest products laboratory general technical report FPL-GTR-113, USDA Forest Service, Madison, WI, USA, pp 2–3
13. Faix O, Meier D, Fortmann I (1990) Thermal degradation products of wood. Gas chromatographic separation and mass spectrometric characterization of monomeric lignin derived product. Holz als Roh- und Werkstoff 48(7–8):281–285
14. Faix O, Meier D, Fortmann I (1990) Thermal degradation products of wood. A collection of Electron-Impact (EI) mass spectra of monomeric lignin derived products. Holz als Roh- und Werkstoff 48(9):351–354
15. Faix O, Fortman D, Bremer J, Meier D (199) Thermal degradation products of wood. Gas chromatographic separation and mass spectrometric characterization of polysaccharide derived products. Holz als Roh- und Werkstoff 49(5):213–219
16. Faix O, Meier D, Fortmann I (1991) Thermal degradation products of wood. A collection of Electron-Impact (EI) mass spectra of polysaccharide derived products. Holz als Roh- und Werkstoff 49(7–8):299–304
17. Collard F-X, Blin J (2014) A review on pyrolysis of biomass constituents: mechanisms and composition of the products obtained from the conversion of cellulose hemicellulose and lignin. Renew Sust Energ Rev 38:594–608
18. Lin Y-C, Cho J, Tompsett GA, Westmoreland PR, Huber GW (2009) Kinetics and mechanism of cellulose pyrolysis. J Phys Chem C 113(46):20097–20107
19. Shen DK, Gu S (2009) The mechanism for thermal decomposition of cellulose and its main products. Bioresour Technol 100(24):6496–6504
20. Bao L, Shi L, Luo H, Kong L, Li S, Wei W, Sun Y (2017) Mechanism of microwave-assisted pyrolysis of glucose to furfural revealed by isotopic tracer and quantum chemical calculations. Chem Sus Chem 10(15):3040–3043
21. Dence CW, Lin SY (1992) Introduction. In: Lin SY, Dence CW (eds) Methods in lignin chemistry. Springer, Berlin
22. Siau JF (1984) Wood structure and chemical composition. In: Transport processes in wood. Springer, Berlin
23. Patwardhan PR, Brown RC, Shanks BH (2011) Understanding the fast pyrolysis of lignin. Chem Sus Chem 4(11):1629–1636
24. Alder E (1977) Lignin chemistry—past present and future. Wood Sci Technol 11(3):169–219
25. Britt PF, Buchanan AC III, Thomas KB, Lee S-K (1995) Pyrolysis mechanisms of lignin: surface-immobilized model compound investigation of acid-catalyzed and free-radical reaction pathways. J Anal Appl Pyrol 33:1–19
26. Custodis VBF, Hemberger P, Ma Z, van Bokhoven JA (2014) Mechanism of fast pyrolysis of lignin: studying model compounds. J Phys Chem B 118(29):8524–8531
27. Custodis VBF, Hemberger P, van Bokhoven JA (2017) How inter- and intramolecular reactions dominate the formation of products in lignin pyrolysis. Chem Eur J 23(36):8658–8668
28. Stolle A, Ondruschka B, Hopf H (2009) Thermal rearrangements of monoterpenes and monoterpenoids. Helv Chim Acta 92(9):1673–1719
29. Goldblatt LA, Palkin S (1941) Vapor phase thermal isomerization of α- and β-pinene. J Am Chem Soc 63(12):3517–3522
30. Gajewski JJ, Hawkins CM (1986) Gas-phase pyrolysis of isotopically stereochemically labeled α-pinene: evidence for a non-randomized intermediate. J Am Chem Soc 108(4):838–839
31. Stolle A, Ondruschka B, Bonrath W (2007) Comprehensive kinetic and mechanistic considerations for the gas-phase behaviour of pinane-type compounds. Eur J Org Chem 14:2310–2317
32. Cowan HJ, Smith PR (1988) Plastics and carpets. In: The science and technology of building materials, Van Nostrand Beinhold Co, New York

33. Rutowski JV, Levin BC (1986) Acrylonitrile-butadiene-styrene copolymers (ABS): pyrolysis and combustion products and their toxicity—a review of the literature. Fire Mater 10(3–4):93–105
34. Braun E, Levin BC (1986) Polyesters: a review of the literature on products of combustion and toxicity. Fire Mater 10(3–4):107–123
35. Paabo M, Levin BC (1987) A review of the literature on the gaseous products and toxicity generated from the pyrolysis and combustion of rigid polyurethane foams. Fire Mater 11 (1):1–29
36. Paabo M, Levin BC (1987) A literature review of the chemical nature and toxicity of the decomposition products of polyethylenes. Fire Mater 11(2):55–70
37. Braun E, Levin BC (9187) Nylons: a review of the literature on products of combustion and toxicity. Fire Mater 11(2):71–88
38. Gurman JL, Baier L, Levin BC (1987) Polystyrenes: a review of the literature on the products of thermal decomposition and toxicity. Fire Mater 11(3):109–130
39. Huggett C, Levin BC (1987) Toxicity of the pyrolysis and combustion products of poly (vinyl chlorides): a literature assessment. Fire Mater 11(3):131–142
40. DeHaan JD (2002) Our changing world. Part 1: furnishings. Fire Arson Investig 52(2):44–45
41. Levin BC (1987) A summary of the NBS literature reviews on the chemical nature and toxicity of the pyrolysis and combustion products from seven plastics: Acrylonitrile–butadiene–styrenes (ABS) nylons polyesters polyethylene polystyrenes poly(vinyl chlorides) and rigid polyurethane foams. Fire Mater 11(3):143–157
42. Levchik SV, Weil ED (2004) Thermal decomposition combustion and fire-retardancy of polyurethanes—a review of the recent literature. Polym Int 53(11):1585–1610
43. Sugimura Y, Nagaya T, Tsuge S, Murata T, Takeda T (1980) Microstructural characterization of polypropylenes by high-resolution pyrolysis-hydrogenation glass capillary gas chromatography. Macromolecules 13(4):928–932
44. Stauffer E (2003) Concept of pyrolysis for fire debris analysts. Sci Justice 43(1):29–40
45. Shapi MM (1990) Thermal decomposition of polystyrene: volatile compounds from large-scale pyrolysis. J Anal Appl Pyrolysis 18(2):143–161
46. Cameron GG (1970) Patterns and problems in the pyrolysis behaviour of synthetic addition polymers. In: The mechanisms of pyrolysis oxidation and burning of organic materials. National Bureau of Standards Special Publication, vol 357. Proceedings of the 4th materials research symposium, 26–29 Oct 1970, Gaithersburg, MD, USA, pp 61–72
47. Moldoveanu SC (2005) Analytical pyrolysis of synthetic organic polymers. In: Techniques and instrumentation in analytical chemistry, vol 25. Elsevier, Amsterdam
48. Wampler TP (1989) Thermometric behavior of polyolefins. J Anal Appl Pyrolysis 15: 187–195
49. Wampler TP, Levy EJ (1986) Effects of slow heating rates on products of polyethylene pyrolysis. Analyst 111:1065–1067
50. Ueno T, Nakashima E, Takeda K (2010) Quantitative analysis of random scission and chain-end scission in the thermal degradation of polyethylene. Polym Degrad Stab 95 (9):1862–1869
51. Prather KR, Towner SE, McGuffin VL, Smith RW (2014) Effect of substrate interferences from high-density polyethylene on association of simulated ignitable liquid residues with the corresponding liquid. J Forensic Sci 59(1):52–60
52. Wampler TP (1999) Introduction to pyrolysis–capillary gas chromatography. J Chromatogr A 842(1–2):207–220
53. McNeill IC (1997) Thermal degradation mechanisms of some addition polymers and copolymers. J Anal Appl Pyrolysis 40–41:21–41
54. Liebman SA, Ahlstrom DH, Quinn EJ, Geigley AG, Meluskey JT (1971) Thermal decomposition of poly(vinyl chloride) and chlorinated poly(vinyl chloride). II. Organic analysis. J Polym Sci A Polym Chem 9(7):1921–1935
55. O'Mara MM (1977) Combustion of PVC. Pure Appl Chem 49(5):649–660

56. Lattimer RP, Kroenke WJ (1980) The formation of volatile pyrolyzates form poly(vinyl chloride). J Appl Polym Sci 25(1):101–110
57. Montaudo G, Puglisi C (1991) Evolution of aromatics in the thermal degradation of poly (vinyl chloride): a mechanistic study. Polym Degrad Stab 33(2):229–262
58. Jackowski JP (1997) The incidence of ignitable liquid residues in fire debris as determined by a sensitive and comprehensive analytical scheme. J Forensic Sci 42(5):828–832
59. Sutherland DA (1999) Fire debris analysis statistics and the use of the latest analytical tools. Can Assoc Fire Investigat J September 11–13
60. Bertsch W, Zhang Q-W (1990) Sample preparation for the chemical analysis of debris in suspect arson cases. Anal Chim Acta 236(1–2):183–195
61. Howard J, McKague AB (1984) A fire investigation involving combustion of carpet material. J Forensic Sci 29(3):919–922
62. Bertsch W (1994) Volatiles from carpet: a source of frequent misinterpretation in arson analysis. J Chromatogr A 674(1–2):329–333
63. Keto RO (1995) GC/MS data interpretation for petroleum distillate identification in contaminated arson debris. J Forensic Sci 40(3):412–423
64. Cavanagh K, Du Pasquier E, Lennard C (2002) Background interference from car carpets—the evidential value of petrol residues in cases of suspected vehicle arson. Forensic Sci Int 125(1):22–36
65. Fanton L, Jdeed K, Tilhet-Coartet S, Malicier D (2006) Criminal Burning. Forensic Sci Int 158(2–3):87–93
66. Tümer AR, Akçan R, Karacaoglu E, Balseven-Odabaşı A, Keten A, Kanburoğlu C, Ünal M, Dinç AH (2012) Postmortem burning of the corpses following homicide. J Forensic Legal Med 19:223–228
67. Sandercock PML (2017) A survey of fire debris casework in Canada 2011–2016. Can Soc Forensic Sci J. http://dx.doi.org/10.1080/00085030.2017.1380979
68. Davies M, Mouzos J (2007) Fatal fire: fire-associated homicide in Australia 1990–2005. Trends Iss Crime Criminal Justice No. 340
69. Ferguson C, Doley R, Watt B, Lyneham M, Payne J (2015) Arson-associated homicide in Australia: a five year follow-up. Trends Iss Crime Criminal Justice No. 484
70. DeHaan JD, Campbell SJ, Nurbakhsh S (1999) Combustion of animal fat and its implications for the consumption of human bodies in fires. Sci Justice 39(1):27–38
71. DeHaan JD, Brien DJ, Large R (2004) Volatile organic compounds from the combustion of human and animal issue. Sci Justice 44(4):223–236
72. DeHaan JD, Taormina EI, Brien DJ (2017) Detection and characterization of volatile organic compounds from burned human and animal remains in fire debris. Sci Justice 57(2):118–127
73. Won D, Magee RJ, Lusztyk E, Nong G, Zhu JP, Zhang JS, Reardon JT, Shaw CY (2003) A Comprehensive VOC emission database for commonly-used building materials. Institute for Research in Construction, Ottawa, Canada. Report No. NRCC-46265, pp 1–7
74. Wells SB (2005) The identification of isopar H in vinyl flooring. J Forensic Sci 50(4): 865–872
75. Hetzel SS, Moss RD (2005) How long after waterproofing a deck can you still isolate an ignitable liquid? J Forensic Sci 50(2):369–376
76. Lentini JJ (2001) Persistence of floor coating solvents. J Forensic Sci 46(6):1470–1473
77. Kataoka H, Ohashi Y, Mamiya T, Nami K, Saito K, Ohcho K, Takigawa T (2012) Indoor air monitoring of volatile organic compounds and evaluation of their emission from various building materials and common products by gas chromatography mass spectrometry. In: Mohd MA (ed) Advanced gas chromatography—progress in agricultural biomedical and industrial applications, InTech Open Science. Available via InTech. http://www.intechopen.com/books/advanced-gaschromatography-progress-in-agricultural-biomedical-and-industrial-applications/stationary-phases. Accessed 5 June 2013
78. Denk P, Velasco-Schön C, Buettner A (2017) Resolving the chemical structures of off-odorants and potentially harmful substances in toys—example of children's swords. Anal Bioanal Chem 409(22):5249–5258

79. Korpi A, Järnberg J, Pasanen A-L (2009) Microbial volatile organic compounds. Crit Rev Toxicol 39(2):139–193
80. Lentini JJ, Dolan JA, Cherry C (2000) The petroleum-laced background. J Forensic Sci 45 (5):968–989
81. Lentini JJ (1998) Differentiation of asphalt and smoke condensates from liquid petroleum distillates using GC/MS. J Forensic Sci 43(1):97–113
82. Coulson SA, Morgan-Smith RK (2000) The transfer of petrol on to clothing and shoes while pouring petrol around a room. Forensic Sci Int 112(2–3):135–141
83. Pitarque M, Vaglenov A, Nosko M, HirvonenA Norppa H, Creus A, Marcos R (1999) Evaluation of DNA damage by the Comet assay in shoe workers exposed to toluene and other organic solvents. Mutat Res 441:115–127
84. Perbellini L, Soave C, Cerpelloni M (1992) [Solvent pollution in shoe factories]. La Medicina del Lavoro 83(2):115–119 [In Italian, English Abstract]
85. Nijem K, Kristensen P, Thorud S, Al-Khatib A, Takrori F, Bjertness E (2001) Solvent exposures at shoe factories and workshops in Hebron City West Bank. Int J Occup Environ Health 7(3):182–188
86. Cherry C (1996) Arsonist's shoes: clue or confusion? In: Proceedings of the American Academy of Forensic Science, Nashville, TN, USA, February 1996
87. Ohkuwa T, Funada T, Tsuda T (2012) Acetone response with exercise intensity. In: Mohd MA (Ed) Advanced gas chromatography—progress in agricultural biomedical and industrial applications, InTech Open Science. Available via InTech. http://www.intechopen.com/books/advanced-gaschromatography-progress-in-agricultural-biomedical-and-industrial-applications/stationary-phases. Accessed 5 June 2013
88. Dormont L, Bessière J-M, Cohuet A (2013) Human skin volatiles: a review. J Chem Ecol 39 (5):569–578
89. Prada PA, Curran AM, Furton KG (2011) The evaluation of human hand odor volatiles on various textiles: a comparison between contact and noncontact sampling methods. J Forensic Sci 56(4):866–881
90. Hawthorne JS, Wojcik MH (2006) Transdermal alcohol measurement: a review of the literature. Can Soc Forensic Sci J 39(2):65–71
91. Montani I, Comment S, Delémont O (2010) The sampling of ignitable liquids on suspects' hands. Forensic Sci Int 194(1–3):115–124
92. Dekeirsschieter J, Verheggen F, Gohy M, Hubrecht F, Bourguignon L, Lognay G, Haubruge E (2009) Cadaveric volatile organic compounds released by decaying pig carcasses (Sus domesticus L.) in different biotopes. Forensic Sci Int 189(1–3):46–53
93. Statheropoulos M, Agapiou A, Spiliopoulou C, Pallis GC, Sianos E (2007) Environmental aspects of VOCs evolved in the early stages of human decomposition. Sci Total Environ 385 (1–3):221–227
94. Magrabi SA, Dlugogorski BZ, Jameson GJ (2002) A comparative study of drainage characteristics in AFFF and FFFP compressed-air fire-fighting foams. Fire Saf J 37(1):21–52
95. Kim AK, Dlugogorski BZ, Mawhinney JR (1994) The effect of foam additives on the fire suppression efficiency of water mist. In: Proceedings of the Halon options technical working conference, Albuquerque, NM, USA, pp 347–355
96. Knappmeyer K, Yoshida S (1997) Detection of extinguishing agents. TIELINE 21(1–2): 21–28
97. Coulson SA, Morgan-Smith RK, Noble D (2000) The effect of compressed air foam on the detection of hydrocarbon fuels in fire debris samples. Sci Justice 40(4):257–260
98. Contreras PA, Houck SS, Davis WM, Yu JCC (2013) Pyrolysis products of linear alkylbenzenes—implications in fire debris analysis. J Forensic Sci 58(1):210–216
99. National Fire Protection Association (2017) NFPA 921 Guide for fire and explosion investigations, Quincy, MA, USA, Section 17.4.2.1
100. Grafit A, Avissar YY, Kimchi S, Muller D (2017) A Preliminary investigation into background interferences in identifying flammable residues from gloves. J Forensic Ident 67 (1):45–59

101. Mann DC, Putaansuu ND (2006) Alternative sampling methods to collect ignitable liquid residues. Fire Arson Investig 57(1):43–46
102. Ettling BV, Adams MF (1968) The study of accelerant residues in fire remains. J Forensic Sci 13(1):76–89
103. Chasteen CE, Hurchins RR, Render ML (1995) Preparation of pyrolysis standards to approximate pyrolysis products observed in fire scenes. In: Proceedings of the international symposium on the forensic aspects of arson investigations, Fairfax, VA, USA, July 31–Aug 4 1995, U.S. Department of Justice Federal Bureau of Investigation, pp 331–334
104. Sandercock PML (2012) Preparation of pyrolysis reference samples: evaluation of a standard method using a tube furnace. J Forensic Sci 57(3):738–743
105. Sferopoulos R (2013) Test burning of carpet and foam and potential interferences in identifying petrol in arson investigation by gas chromatography/mass spectrometry. PhD Thesis, Victoria University, Melbourne, Australia
106. Johansen NG, Ettre LS, Miller RL (1983) Quantitative analysis of hydrocarbons by structural group type in gasolines and distillates. I: Gas chromatography. J Chromatogr 256:393–417

Mark Sandercock retired from the National Centre for Forensic Science, Royal Canadian Mounted Police (RCMP), in 2018, after working for 27 years in the field of forensic trace evidence. During his career with the RCMP, he worked not only as Trace Evidence Scientist, including testifying numerous times as an expert witness in court, but also held the positions of National Program Technical Leader and, later, Manager of the Trace Evidence Service at the Edmonton Laboratory. He has published 42 forensic science articles in peer-reviewed journals, 22 of which are related to forensic analysis of ignitable liquids and fire debris. In addition, he has contributed to another published book on fire debris analysis and has also presented a review on fire debris analysis at a Forensic Science Symposium hosted by INTERPOL.

Chapter 4
Vegetable Oil, Biodiesel and Ethanol Alternative Fuels

Douglas Byron

Learning Objectives

- Understand the basic concept of fatty acids: where they come from and how they are refined and manufactured for consumer use.
- Introduce the types of products that contain vegetable oils and alternative fuels.
- Provide a basic understanding of analysis and reporting for vegetable-based products.

4.1 The Importance of Looking Beyond

Most fire debris examiners are trained to extract and identify traditional petroleum-based liquids from debris for criminal and civil litigation purposes. New technologies and the push for more environmentally friendly alternatives have changed the nature of the fuels which examiners can expect to see in their evidence. The tendency for some vegetable-based oils to spontaneously ignite further broadens the range of liquids that may be encountered by fire debris examiners. Arise in the use of vegetable-based oils and alternative fuels in recent years has forced the field of fire debris analysis to look beyond what it classically considered ignitable liquids. Understanding the basis of these fuels, how they are manufactured, and the effects of fire and environmental conditions on each type of liquid become paramount.

D. Byron (✉)
Forensic and Scientific Testing, Inc. (FAST Inc.), Lawrenceville, GA, USA
e-mail: dbyron@fast-lab.com

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_4

4.2 Vegetable Oils (VOs) and Vegetable Oil Residues (VORs)

Vegetable oils (VOs) are oils that are typically derived from plants and can range from cooking oils, such as sesame and olive oils, to drying oils, such as linseed and tung oils [1]. When found on debris samples, they are referred to as **vegetable oil residues (VORs)**. VOs are not the typical liquids that come to mind in the discussion of fire debris analysis. They are not as easily ignited as the petroleum-based ignitable liquids, nor are they generally used to intentionally start a fire. This may be, in part, why many criminal laboratories do not routinely screen samples for VOs [2]. The screening for VOs, however, can be useful for investigators trying to determine the cause of a fire, as it may corroborate claims of a cooking fire, spontaneous ignition, or support details provided during witness statements or confessions when they are involved in criminal cases.

4.2.1 Vegetable Oil Compositions

Fatty acids (FAs) are naturally occurring aliphatic chains, usually containing ten or more carbon atoms, with a carboxylic acid at one terminus [2]. When found alone, they are referred to as **free fatty acids (FFAs)**. Three FFAs can be esterified with a glycerin molecule, as shown in Fig. 4.1. In this form, they are called **triglycerides, triacylglycerides (TAGs)**, or more commonly fats or oils [3]. FAs can be saturated, monounsaturated, or polyunsaturated. Unsaturation refers to the presence of double bonds; for example, monounsaturated FAs have one double bond. **Polyunsaturated FAs (PUFAs)** have two or more in their carbon chain. When FAs contain more than one double bond, the double bonds are normally separated by a methylene group ($–CH_{2-}$) [2, 4].

Saturated FAs are relatively linear in nature and can stack to form a crystalline structure [2]. As a result, they are typically solid at room temperature. The double bond in unsaturated FAs, particularly the cis-isomers, forms a bend in the carbon

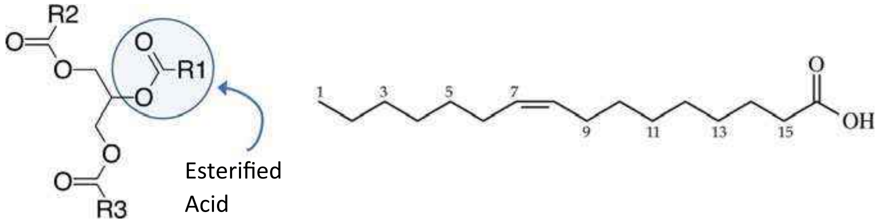


Fig. 4.1 Left: chemical structure of a triglyceride (TAG). Right: chemical structure of a free fatty acid (FFA) [3]

chain [5]. This prevents the molecules from being able to stack on each other, causing them to be liquid at room temperature.

Most literature uses a shorthand nomenclature for FAs to indicate the length of the carbon chain and the number of double bonds. For example, oleic acid, shown in Fig. 4.2, has an 18-carbon chain with one double bond and is written as C18:1 (n-9) [3, 5, 6]. The "C" represents the number of carbons in the FA including the carboxylic group, the number after the colon is the number of double-bonded carbons present, and the number in parenthetical is the number of carbon atoms from (and including) the terminal methyl group where the first double bond is located. Typically, this shorthand is shortened even further to C18:1. As another example, the FA in Fig. 4.1, known as palmitoleic acid, would be written as C16:1 in the abbreviated shorthand.

4.2.2 Vegetable Oils

Regardless of their origin, all TAGs derived from biological sources, animal or vegetable, are considered vegetable oils for the purpose of fire debris analysis. Naturally occurring FAs tend to have double bonds in the cis-position, and their oils and fats can contain ten to fifteen different FAs in various amounts [4]. Animal products tend to contain saturated FAs and are found in solid forms, such as lard. The exception is some fish oils which, while saturated, are a liquid at room temperature [2]. Cooking oils are refined from plant-based sources such as corn,

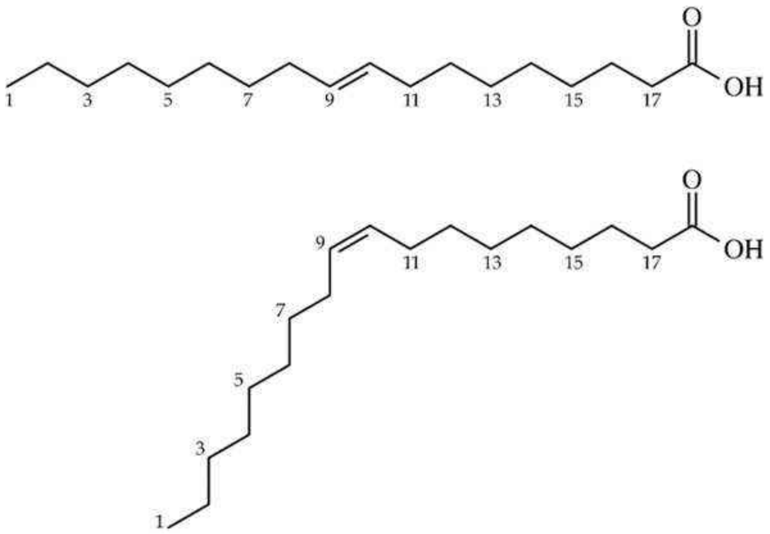


Fig. 4.2 Examples of fatty acid confirmations. Top: trans-C18:1(n-9), elaidic acid. Bottom: cis-18:1(n-9), oleic acid. To conserve space, the cis-conformation is typically drawn flat [3]

soybean, and olive plants. Typically, vegetable oils used for cooking are composed of FAs of a lower degree of unsaturation and are not prone to self-heating. However, when vegetable oils with a lower tendency to self-heat are subjected to a heat source, such as a cloth dryer, the reaction can begin and lead to spontaneous ignition [2, 7].

4.2.3 Drying Oils

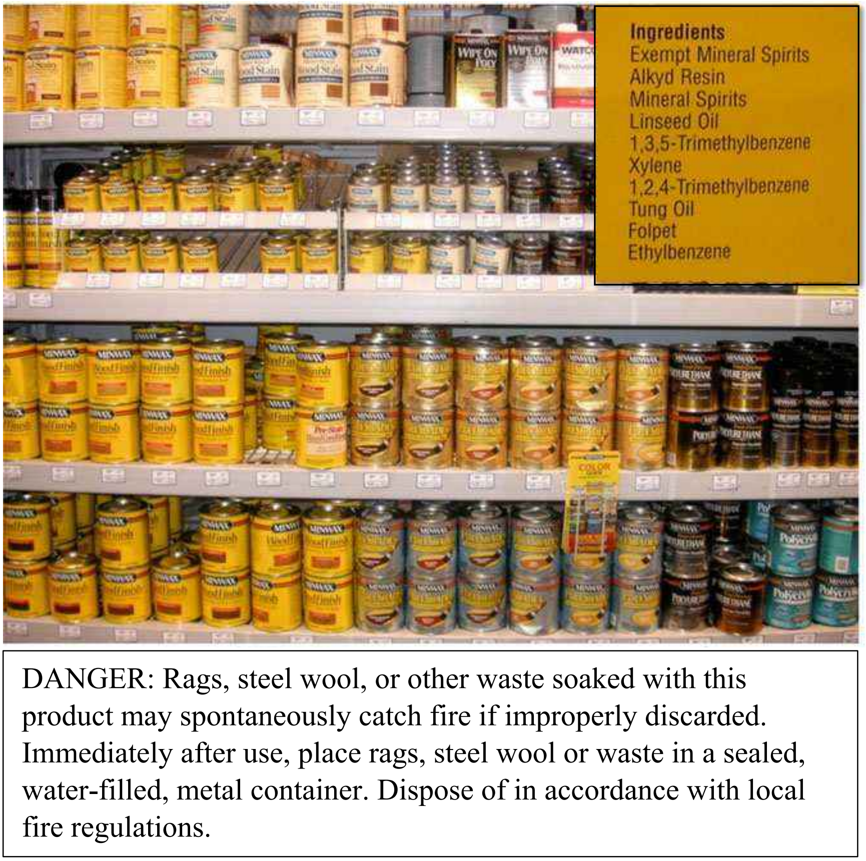
Unsaturated oils such as tung, boiled linseed, and dehydrated castor oils are used as **drying oils**. They can undergo oxidative polymerization to form hard films, which makes them valuable additives for surface oils, stains, and printing inks [8]. The tendency for these oils to spontaneously ignite has been well documented in history. Some of the earlier research started when the Russian frigate *Marie* caught fire in 1781. Believing it to have been caused by storing hammocks soaked with stain (hempseed oil and pine soot), Count Ivan Tschernichev, Vice President of the St. Petersburg Admiralty College, commissioned a study to determine the self-heating properties of oil-soaked materials. By the 1940s, the methods for understanding the reaction when dealing with non-uniform temperatures within the material were uncovered by Russian researcher David Frank-Kamenetskii [9]. While known to happen (Fig. 4.3), the mechanism behind it has only been recently uncovered.

Linseed oil is a common drying oil that is known to have a high propensity for self-heating. Modern “boiled” linseed oil has added catalysts, which can include lead-containing compounds, to increase the rate of autoxidation of the FAs, thus increasing the rate of polymerization and the likelihood of spontaneous combustion [10].

Certain formulations of drying oils contain more than TAGs and catalysts. Some products, such as wood stains and drying oil (as in Fig. 4.3), also contain traditional ignitable liquids. These formulations can also spontaneously ignite under the correct conditions. Because these formulations contain ignitable liquids to dilute the oils, they provide additional information that can be used for characterization during the analysis. While brand identification may not be possible, characteristics of these formulations can provide additional information that can be used to narrow possible sources.

4.2.4 Spontaneous Ignition

Unlike **autoignition**, where radiant heat causes neighboring materials to ignite, spontaneous ignition is a biological or chemical process where materials ignite in the absence of an external heat source because of self-heating [2]. Linseed oil on wadded up cotton rags, oily rags that have been laundered, and recently varnished floors that are subsequently sanded are examples where this type of ignition has



Ingredients
Exempt Mineral Spirits
Alkyd Resin
Mineral Spirits
Linseed Oil
1,3,5-Trimethylbenzene
Xylene
1,2,4-Trimethylbenzene
Tung Oil
Folpet
Ethylbenzene

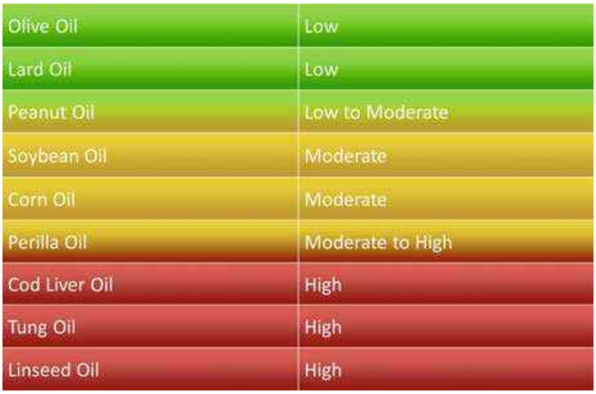
DANGER: Rags, steel wool, or other waste soaked with this product may spontaneously catch fire if improperly discarded. Immediately after use, place rags, steel wool or waste in a sealed, water-filled, metal container. Dispose of in accordance with local fire regulations.

Fig. 4.3 Examples of drying oils found in a local hardware store. Top left: image of the stains and other products containing drying oils. Top right: ingredient list on the label of a stain. Bottom: spontaneous combustion warning on a product

occurred. Fish oils and fish meal also have a high tendency to self-heat [3]. Table 4.1 lists examples of oils with different propensities for **spontaneous ignition** [11]. These fires rarely have witnesses, produce copious amounts of smoke and odors, and can take several hours to ignite (up to 80 h) [12]. The acrid odors and discoloration of materials associated with spontaneous ignition fires are a result of the same chemical reaction that caramelizes food, called the **Maillard reaction**. The FAs react with the matrix to produce the charring and chemicals with these distinctive odors [13].

The tendency for self-heating is directly related to the unsaturation level [1, 2, 10]. Double bonds present in FAs reduce the C–H bond strength on neighboring carbon atoms. As a result, less energy is required to oxidize this bond and remove the hydrogen [6, 10]. This **oxidation** process releases heat that, if not dissipated,

Table 4.1 Different oils and their self-heating tendencies [11]



Olive Oil	Low
Lard Oil	Low
Peanut Oil	Low to Moderate
Soybean Oil	Moderate
Corn Oil	Moderate
Perilla Oil	Moderate to High
Cod Liver Oil	High
Tung Oil	High
Linseed Oil	High

can cause further oxidation of the FA and potentially spontaneous ignition. The more double bonds present in the FA, the more unstable it is [14]. For example, C18:3 has a reaction rate 25 times that of C18:1, while C18:2 has a reaction rate approximately 10 times that of C18:1 [2, 15]. Oils having high percentages of 18:3 are the most prone to spontaneous ignition. Oxidization of the oils can also be accelerated by other means. Heat, sunlight, and metallic driers accelerate the oxidation process [1, 10].

Antioxidants are added to some vegetable oil-based products to prevent the degradation of FAs. When antioxidants such as citric acid, tocopherol, butylated hydroxyanisole (BHA), and butylated hydroxytoluene (BHT) are present, free radicals react with the inhibitors instead of reacting with the FAs [2, 8, 10]. The period of time when the antioxidants are being consumed is called the **induction period** [6, 10]. Once antioxidants, natural and added, have been depleted, the autoxidation of FAs begins.

The oxidation of the FA is an exothermic process; however, the reaction does not guarantee a material will ignite. The tendency of a material to undergo spontaneous ignition depends on the initial temperature, rate of heat generation within the oil, the rate of heat dissipation to the surrounding material, and the availability of oxygen as well as the size, shape, and nature of the fuel package [2, 16]. For spontaneous combustion to proceed, oils need to be on a solid, porous medium so oxygen will be in contact with the oil throughout the heating process [12]. The support medium, such as 100% cotton rags, does not have to be combustible so long as it forms a rigid char when heated. An example of this is seen in laundry fires which involve cooking oils, where the heat of the dryer provides the heat needed to initiate the reaction. Materials that form a fluid mass when heated are not likely to allow spontaneous combustion, and bulk liquids will not spontaneously combust without the aid of catalytic reactions.

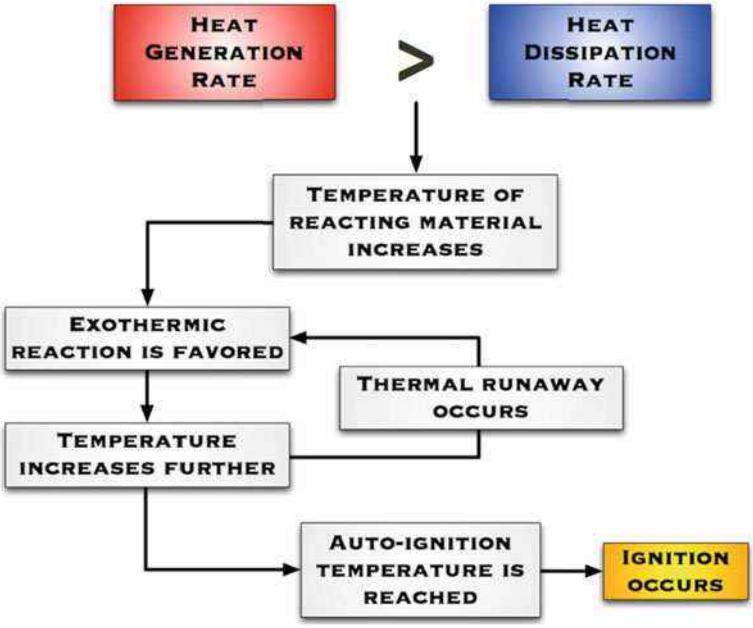

HEAT GENERATION RATE
>
HEAT DISSIPATION RATE
TEMPERATURE OF REACTING MATERIAL INCREASES
EXOTHERMIC REACTION IS FAVORED
THERMAL RUNAWAY OCCURS
TEMPERATURE INCREASES FURTHER
AUTO-IGNITION TEMPERATURE IS REACHED
IGNITION OCCURS

Fig. 4.4 Flow diagram showing the steps leading to spontaneous ignition

When the oil is on a material which does not allow for adequate heat dissipation, the thermal oxidation reaction can cause the temperature to climb (Fig. 4.4). For every increase in 10 °C, the reaction rate doubles over the previous rate [17]. An exponential increase in the heat generation, referred to as **thermal runaway**, can occur when the heat generated speeds further oxidation reactions [2]. If the thermal oxidation reaction continues, the temperature can increase until it reaches the flame point of the support medium, leading to ignition.

4.2.5 Collection and Storage of Vegetable Oils

When a fire is suspected of being caused by a self-heating reaction, any remaining VORs can be further degraded by heat, oxygen, and water [10, 18]. The evidence to be tested (liquid samples, material from the lint trap, clothes from the dryer, nearby box of rags, etc.) should be collected in a vapor-tight container and stored under cold conditions, preferably a freezer, to help preserve any remaining VORs and reduce further degradation [10]. As seen in Fig. 4.5, FAs stored at room temperature can oxidize over time, resulting in the saturation of the double bonds. The higher number of double bonds a FA has, the easier it is to oxidize. This results in an overall reduction in PUFA levels in the oil over time.

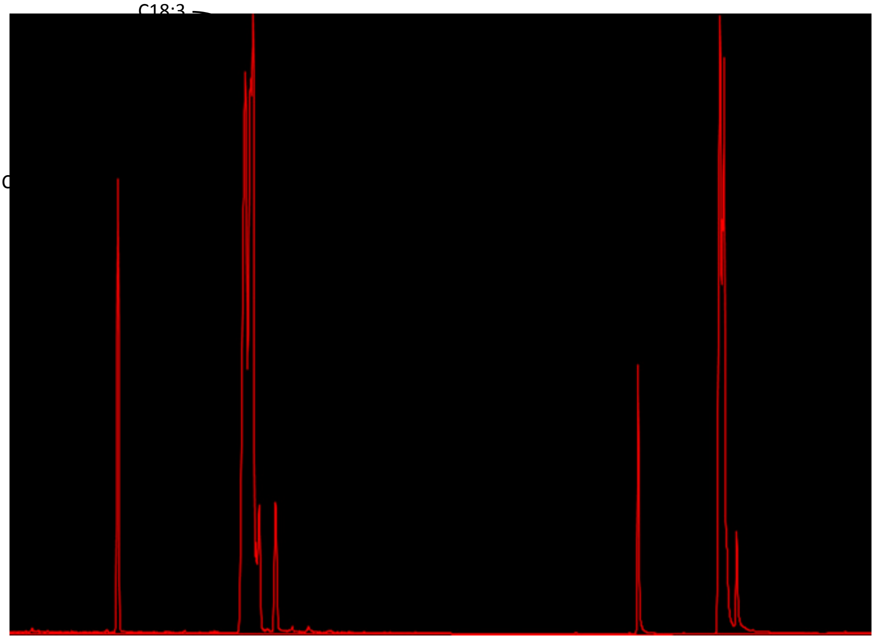


Fig. 4.5 Image on the left shows an expanded chromatogram of a product containing FAs. Image right is the same product analyzed nine years later. Product was stored at room temperature and transesterified for analysis. C18:3 is present in the degraded sample; however, the abundance is significantly less than the fresh product

When possible, a **comparison sample** of suspected oils should be sent for testing as well [6]. Protected from the effects of the fire, these liquid comparison samples can offer information as to what an occupant or contractor was using near the time of the fire and provide a more accurate representation of the original FA profile.

Establishing early communication with evidence recovery personnel and original investigators is important for ensuring proper treatment of evidence suspected to contain VORs. Recovered evidence should be taken to the laboratory as soon as practical and evidence-receiving staff should be notified upon submission that the evidence is suspected to contain FAs. VORs are also subjected to the same **microbial degradation** issues as conventional ignitable liquids [18].

4.2.6 *Extraction and Analytical Considerations*

From an investigative standpoint, VOR analysis is typically geared toward identifying fatty acids that may have a tendency to self-heat and could potentially result in spontaneous ignition. The analytical scheme chosen as well as the results and conclusions that can be drawn from testing are dependent upon what is submitted to the laboratory for testing. Factors affecting the end conclusions include the nature of the oil; degradation effects of light, oxygen, humidity, and microbes; thermal degradation effects; the matrix on which the VOR was applied; and the extraction methods used [6, 10, 19].

4.2.6.1 Ignitable Liquid Analysis

ILR testing is the logical start in the analytical scheme for either neat liquids or debris samples [10]. VORs have boiling points above 300 °C, which makes **passive headspace concentration** an unacceptable recovery method in debris; however, some products contain traditional ignitable liquids that can easily be recovered by passive headspace concentration [10, 14, 20]. While fire scenes can thermally degrade oils, the typical 16-h exposure at 65 °C during extraction of petroleum-based ignitable liquids will not destructively alter the sample [6, 20]. Occasionally, FFAs can be recovered in headspace extraction, offering an examiner an indication that VORs may be present. Depending on the circumstances of the case and the type of matrix, further analysis for possible VORs may be necessary. An alternative for ILR recovery is **solvent extraction** [21, 22]. While solvent extraction is not generally used for ignitable liquid testing for reasons discussed in Chap. 2, the use of solvents such as pentane can effectively recover both the ILR and the VOR fractions [10].

4.2.6.2 GC-MS Considerations

GC-MS is the most common method for characterizing VOs in liquids and VORs in debris samples. The preparation of samples for VO analysis, however, differs from standard ignitable liquid analysis. Both bound and free FAs are too heavy and too reactive with traditional fire debris columns to be analyzed successfully using fire debris methods, so they are converted to **fatty acid methyl esters (FAMEs)**, which are more volatile [10, 14].

Neat liquids may be diluted in a solvent and then converted to FAMEs in a process known as derivatization. Debris samples, however, must be solvent extracted first. The resultant extract is then derivatized to form FAMEs. Several organic solvents are suitable for this purpose, including ethyl and diethyl ethers, pentane, hexane, heptane, and cyclohexane. The recovered extract is then derivatized with ~2 N potassium hydroxide (KOH) in methanol [10]. The methanol converts bound or free fatty acids into FAMEs. For example, the TAG in Fig. 4.1 would be converted to a glycerin molecule and three FAMEs (FAs which terminate with—COOMe instead of—COOH). This technique, known as **base-catalyzed transesterification**, is a simple technique that provides good reproducibility and is inexpensive to perform [14] (Fig. 4.6).

The methanol–organic solvent mixture separates, and the upper organic layer is removed for GC-MS analysis. If the sample is not concentrated enough, the

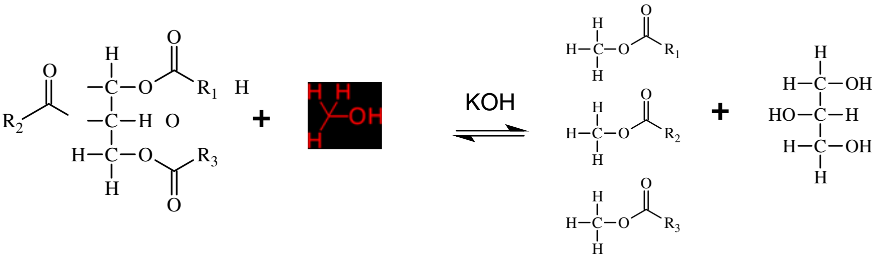


Fig. 4.6 Reaction for base-catalyzed transesterification [3]

derivatized extract can be evaporated at room temperature. The application of heat should be avoided, as it can further oxidize and degrade the sample, which will alter the FAME profile [10].

Unlike petroleum products, which can produce complex patterns of peaks in the TIC, derivatized VOs will produce a relatively simple TIC with several peaks. Traditional nonpolar fire debris columns, such as DB-1 and DB-5, can be used when full separation and quantification of the individual FAMEs are not needed [3, 10]. Some examples of FAME profiles using these columns are shown in Fig. 4.7. While these columns do not provide baseline separation for some of the

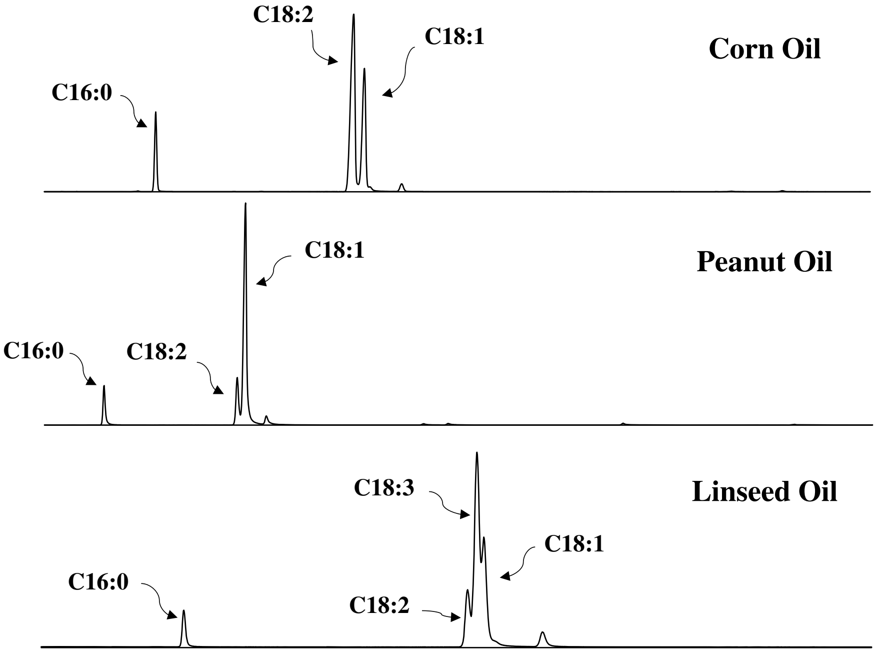


Fig. 4.7 Examples of FAME profiles of oils expanded to show predominant peaks. Peak 1 is C16:0, Peak 2 is C18:2, Peak 3 is C18:1, and Peak 4 is C18:3

more common FAMEs, the compounds can be resolved sufficiently to allow for identification using mass spectrometry. To obtain optimal separation of the FAMEs by GC-MS, the instrument can be equipped with a polar column (such as a DB-Wax, HP-Wax, Supelco SP2380) [3]. These polar columns are designed specifically for the separation of FAMEs [3, 10]. Columns such as DB-23 also provide efficient separation of complex FAME profiles and can provide some separation between cis- and trans-isomers.

FAMEs create reproducible fragmentation patterns when EI-MS is used. Two particularly useful ions are produced by cleavage of the C–C bond next to the ester. This C–C bond can undergo a McLafferty rearrangement and produce a singly charged radical cation with *m/z* 74 (Fig. 4.8) [18]. The resonance-stabilized acylium ion has *m/z* 59, which results from the alpha cleavage of the C–C bond. While of lower abundance than the McLafferty rearrangement, the infrequent appearance of the *m/z* 59 ion in debris makes it also of value [18]. Along with a loss of 32 amu from the loss of methanol, these ions provide an easy way to confirm a FAME is present [23]. These ions are also useful in an EIP similar to those discussed in Chap. 2 to assist examiners in screening data rapidly. With the molecular weight, examiners can also calculate the number of carbons, hydrogens, and oxygens present; however, the location of double bonds, branch points, and ring structures is difficult to determine and is generally beyond the scope of the investigation [23].

EIPs can also be created using the molecular weights of various FAMEs. Table 4.2 lists some of the molecular weights that can be used to rapidly screen for

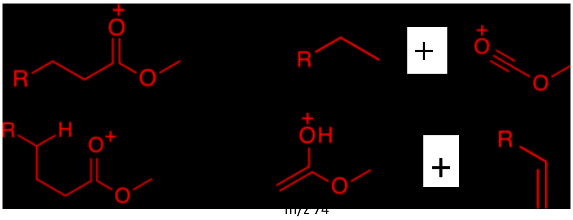


Fig. 4.8 Top: alpha cleavage of the C–C bond results in a resonance-stabilized acylium ion (m/z 59). Bottom: McLafferty rearrangement results in a radical ion (m/z 74) [18]

Table 4.2 Common fatty acids and the molecular weights of the resulting methyl esters [3]

FA Designation	MW (amu)	FA Designation	MW (amu)
C6:0	130	C18:1	296
C8:0	158	C18:2	294
C10:0	186	C18:3	292
C12:0	214	C20:0	326
C14:0	242	C22:0	344
C16:0	270	C24:1	342
C16:1	268	C24:0	372
C18:0	298	C24:1	370

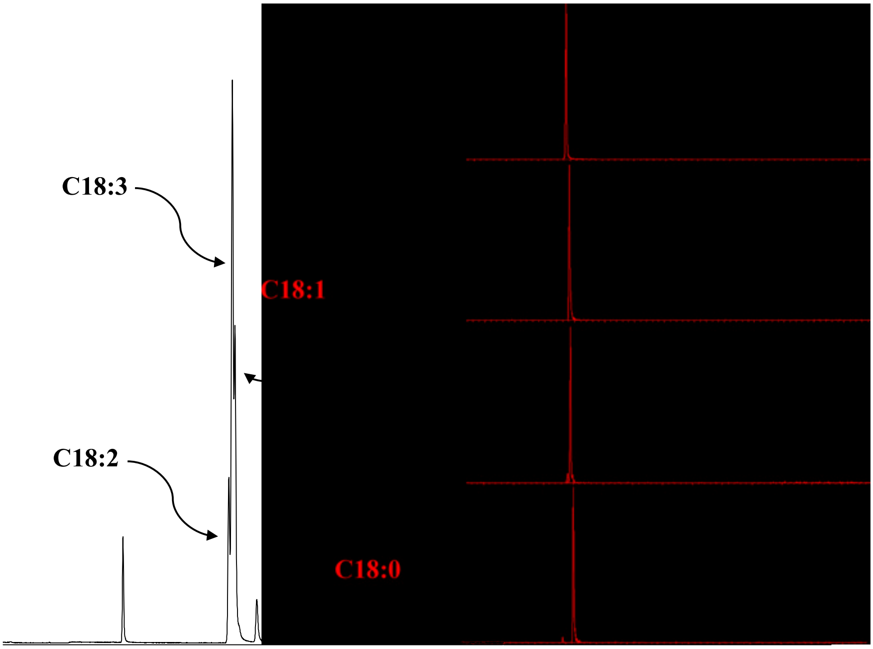


Fig. 4.9 Left: TIC of linseed oil. Right: extracted ion chromatograms (EICs) for various C18:X FAMEs [3, 10]

FAMEs [10]. A series of extracted ion chromatograms representing the molecular weights of FAMEs in linseed oil is shown in Fig. 4.9.

4.2.6.3 Data Interpretation

Analysis of the PUFA content by GC-MS can inform the examiner of the oil's tendency toward self-heating based on the FA content, as shown in Fig. 4.7. With a larger relative percentage of PUFAs, corn oil has a higher tendency to self-heat than peanut oil. Linseed oil, which contains a relatively large proportion of C18:3, will spontaneously ignite under favorable conditions. This information is not, however, enough to state unequivocally that a fire could have occurred via spontaneous ignition. For example, many different formulations of linseed oil are currently marketed to customers for a variety of uses and all will contain similar PUFA profiles; not all linseed oil is prone to spontaneous ignition, however [6]. Some forms contain additives that contribute to the tendency to self-heat [2]. These additives may not be detected using traditional fire debris methods. The mixture of the PUFA profile and physical tests can demonstrate if the oil is truly capable of self-heating to the point of ignition and allows the examiner to conclude that the oil in question can cause spontaneous ignition.

It is also important to remember that the PUFA profile in a debris sample is indicative of what FAs are present at the time of analysis but may not be the same as what was present before the fire started. Once involved in a fire scene, the original oil may be thermally degraded [2, 10]. Heat speeds up the oxidation of the sample and can lead to skewed PUFA profiles that differ from the original oil. As shown in Fig. 4.5, when oils degrade, the FAs present become more saturated than their original composition. The more unsaturated the FA, the more likely it is to be oxidized [1, 10].

Depending on the needs of the submitter, the nature of the samples submitted, and the capabilities of the laboratory, additional testing may be performed. Other tests used to characterize VOs include iodine value, saponification value, acid value, and Mackey (tendency toward self-heating) tests [2]. The **Mackey test** can be modified to test ability of the oil to self-heat to the point of ignition [7]. In this test, oil is applied to cotton rags and placed into a container to provide necessary conditions for thermal runaway. The reaction is monitored for fire indicators such as smell, white smoke, and, eventually, flames. The use of thermocouple data loggers can provide a digital graph for documentation purposes. To speed the reaction, the set up can be placed initially in an isothermal oven and then removed to a location that allows for easier monitoring and extinguishing after completion.

4.2.6.4 Bringing It All Together

Cases where spontaneous combustion or VORs are suspected require examiners to incorporate many considerations before reaching a conclusion. Relative proportions of saturated, monounsaturated, and polyunsaturated FAs present in a sample form the base of information for reporting about a sample's tendency to self-heat. The relative proportions of the classes of FAs can be estimated using their molecular weights. Examiners must also consider the possibility the sample has undergone degradation and may not have the same relative ratios as the original oil [3]. Since FAs degrade to their more saturated forms, the original oil will never be more saturated than what was detected during testing [10].

It is also imperative that laboratories and analysts are aware of the products commonly found in households which are known to contain FAs and VORs. Even when not required to generate the report, these considerations become important when communicating to customers the implications associated with the reported conclusions.

4.2.7 Reporting

The breadth of the conclusions that can be reached is based on the testing performed. If no ignition testing was done, the results should be limited to discussion of the fatty acids present. Examples include [10, 22]:

- No fatty acids were identified.
- Fatty acids were identified: saturated with no tendency to self-heat.
- Fatty acids were identified: monounsaturated with a very low tendency to self-heat.
- Fatty acids were identified: No polyunsaturated fatty acids were detected, indicating little to no tendency of self-heating.
- Fatty acids were identified: low amount of polyunsaturated fatty acids present, indicating a low to moderate tendency of self-heating.
- Fatty acids were identified: A large amount of polyunsaturated fatty acids were identified, indicating a high tendency to self-heat.

Degradation due to heat, water, microbial action, etc., may make it impossible for examiners to correlate saturation levels to the original liquid [6]. When no or low PUFAs are identified, it does not eliminate the possibility that a substance with higher degree of unsaturation with a corresponding tendency to self-heat was present before the fire. Since degradation of VORs presents a reduction in the PUFA level of the oil, the reported results represent the lowest possible tendency for an oil to self-heat. It does not preclude the possibility that the original VOR, prior to the fire incident, had a higher tendency toward self-heating. Conversely, the presence of a relatively large proportion of PUFAs does not necessarily mean that a self-heating reaction occurred.

If the Mackey or modified Mackey test demonstrates the oil is capable of self-heating, especially when it progresses to the point of ignition, then the conclusions include discussion of the tendency of the oil to self-heat and possibly result in spontaneous ignition.

4.3 Alternative Fuels

While vegetable oils require different techniques than traditional fire debris analysis, the analysis of alternative fuels, including vegetable oil-based biodiesel and ethanol fuels, uses familiar fire debris methods. The main difference is the composition of the liquids being analyzed.

Traditional petroleum-based fuels, such as gasoline and diesel, are easy to produce and readily available, but they produce high carbon emissions, pollute the environment, and have a finite supply [1, 24]. **Non-traditional vehicular fuels** have been around for a long time. They have ranged from steam and electrical sources to more obscure fuels like wood smoke. The Alternative Motor Fuels Act, passed in 1988, provided credit toward auto manufacturers who produced alternative fueled vehicles, including engines which operated on propane, natural gas, and flexible fuel designs [25].

Changes in engine requirements and legislative measures have led to changes in the gasoline standards over time. The Clean Air Act Amendments of 1990 eliminated lead from gasolines [26]. In addition, it required an oxygenated additive to be blended into conventional, reformulated, and oxygenated gasolines. Methyl tert-butyl ether (MTBE) was initially used to oxygenate gasolines; concerns with groundwater contamination, however, led US states to start banning its use [25]. The search for a more environmentally friendly and sustainable alternative led to the reemergence of alternative fuels.

The Energy Policy Act of 2005 removed the oxygenate mandate for reformulated gasolines and required the use of renewable fuels [26]. These fuels are a more sustainable source of energy, cleaner burning, more environmentally friendly, and produce fewer carbon monoxide and toxic emissions [1, 24]. This act, along with the ban on MTBE, increased the use of ethanol in gasolines. The move toward alternative vehicular fuels was given an additional push from the Energy Independence and Security Act (EISA) of 2007, which mandated the increased use of biofuels to a level of 36 billion gallons by 2022 [25–27]. Two of the most common types of alternative vehicle fuels available today are ethanol-based fuels, such as E85, and vegetable oil-based biodiesel.

As non-traditional fuels become cost effective to produce and more available, the likelihood of seeing these products during a fire investigation increases. Fire debris examiners need to be aware of emerging fuels, methods of analysis, interpretation of the data as well as how to report them accurately.

4.3.1 Biodiesel

While working on developing his internal combustion engine in the late 1800s, Rudolf Christian Diesel used petroleum-based fuels such as kerosene. In 1900, when he demonstrated its operation during the World Exhibition in Paris, he operated it using peanut oil. Believing in the use of vegetable oils as a fuel source, Diesel theorized they would become as important as petroleum products [28]. Patents obtained in the 1940s by E.I. DuPont and Colgate-Palmolive-Peet provided the basis for the production methods still in use today [24]. Recognizing biodiesel as an alternative fuel in the Energy Policy Act of 1992 (amended in 1996), the Energy Conservation and Reauthorization Act of 1998 added B20 biodiesel to the list of acceptable alternative fuels [1, 29].

Biodiesel (B100) is defined by ASTM D6584 as a "fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats" and can be produced from clean vegetable oils, animal fats, and recycled cooking oils which have been processed to convert their FAs to FAMEs [30, 31]. Shorthand abbreviations of BXX show the percentage of biodiesel present in the fuel [28]. For example, **B20** represents a blended biodiesel product containing 20% biodiesel and 80% petroleum-based fuels, such as diesel, kerosene, jet A, JP8, and heating oils [1]. When the fuel is comprised of only biodiesel, it is referred to as **B100**.

Containing 11% oxygen by weight and having a higher **cetane number**, B100 provides a more complete combustion than traditional diesel and reduces emissions.

Traditional diesel fuels must have a cetane number of at least 40, however, ASTM has set a limit of 47 for all B100 fuels. The higher the cetane number, the better cold start properties the fuel has and the less likely it is to form white smoke. Since plants fix CO_2 to generate carbon-based products and B100 biofuel can be produced from plant-derived feedstocks, the burning of biodiesel blends can have a net overall reduction in CO_2 compared to the burning of standard petroleum fuels [1]. The greater the percentage of biodiesel in the fuel, the larger the reduction.

Historically, traditional diesel contained sulfur to provide a lubricating effect for engine parts. However, current Environmental Protection Agency (EPA) requirements dictate that no more than 15 ppm sulfur be present in diesel fuel to help reduce toxic emissions. The use of this low-sulfur fuel has led to premature fuel pump failure and expensive engine repairs. The addition of biodiesel to ultra-low-sulfur diesels, even as little as 1–2%, helps add lubrication back to the fuel [1]. These low blend biofuels can be marketed and labeled as traditional diesel products. B20, the most common blend marketed in the USA, can be used in diesel engines without modification. This alternative fuel balances the requirements for clean air standards, cost-effectiveness, and performance. B20 can also be stored and pumped using the same equipment found in traditional diesel tanks [1].

The higher cetane number of B100 is thought to lead to quieter engine operation and easier starting; however, the use of B100 is not without its issues. The use of fuels containing high percentages of biodiesel can cause wear on engine components and lead to premature engine failure [1].

4.3.2 Biodiesel Refining

Biodiesel can be produced from a variety of **feedstocks**. The production process is simple, rapid, and cost effective. The FA composition of the feedstock affects the final properties of the biodiesel. Saturated fatty acids from feedstocks, such as hydrogenated frying oils and chicken fat, produce a fuel with a higher cetane number and more stability than those produced from polyunsaturated fatty acids. Biodiesel has been refined from the following sources [1]:

- Animal fat: edible and inedible tallow, lard, white and yellow grease, poultry fats, and fish oils
- Vegetable oils: mustard, palm, coconut, peanut, olive, sesame, safflower, soy, corn, canola, sunflower, rapeseed, and cottonseed
- Used/recycled oils: trap greases and used cooking oils
- Microorganisms: algae, fungi, bacteria, molds, and yeast.

As an underivatized vegetable oil, **straight run vegetable oil (SVO)** has a higher viscosity than diesel fuel. As a result, in cooler temperatures, it is prone to gelling and causes ring sticking, heavier engine deposits, and other maintenance issues. This makes it less than ideal for routine fuel use [1]. To counter these effects, the fatty acids are transesterified to produce FAMEs.

The most common commercial method is base-catalyzed transesterification, due to the low temperature and pressure requirements [28]. This is the same derivatization method discussed earlier for the preparation of vegetable oils for analysis. It produces fewer side reactions than acid-catalyzed transesterification and does not require chemically resistant materials. **Acid-catalyzed transesterification** can be performed, but the reactions are more difficult than base-catalyzed transesterification. The reaction takes several hours at temperatures over 100 °C, and the highly acidic environment requires the use of chemically resistant materials [1, 28]. In addition, the presence of any water can lead to carboxylic acid formation instead of methyl esters [32]. The carbonyl group of the ester is first protonated, cleaving the glycerin. The resulting carbocation then forms a new ester on the FFA to produce the FAME and regenerates the acid catalyst. Bronsted acids, such as HCl, BF_3, H_3PO_4, and H_2SO_4, can work; however, due to the costs involved, sulfuric acid is most frequently used [33].

Regardless of the method used, the end result is FAMEs and glycerin. With respect to fuel production, this remaining glycerin after transesterification is considered waste [28]. The glycerin is removed, methanol is washed from the crude biodiesel fuel, and the methyl esters are neutralized.

4.3.3 Analytical Considerations, Data Interpretation, Classification, and Reporting of Biodiesel

Liquid samples can be analyzed in the same way as traditional petroleum liquids [19, 28]. The abundance of the FAME peaks increases with their increasing concentration in the blend (Fig. 4.10). While most biodiesel fuels will have FAMEs visible in the TIC, B5 biodiesel does not show the presence of FAMEs in the TIC until the sample has been highly weathered [18]. While they may be marketed as traditional diesel fuels, the presence of FAMEs in low percentage blended products can be identified using extracted ion chromatograms (see Sect. 4.2.6).

As with traditional petroleum-based ignitable liquids, the presence of matrices complicates sample preparation. As a blended diesel product, biodiesel is expected to remain on substrates, which increases the likelihood of recovery [28]. While traditional recovery methods work well, depending on the information needed, additional techniques may be required. Differences in the vapor pressures of the various components coupled with competitive adsorption on the carbon strip lead to an underrepresentation of the FAMEs compared to the diesel (Fig. 4.11) [19]. As a result, biofuels extracted with passive headspace concentration are subjected to the same displacement issues seen in petroleum-based products. Higher oven temperatures can increase the recovery of the FAMEs [19, 34].

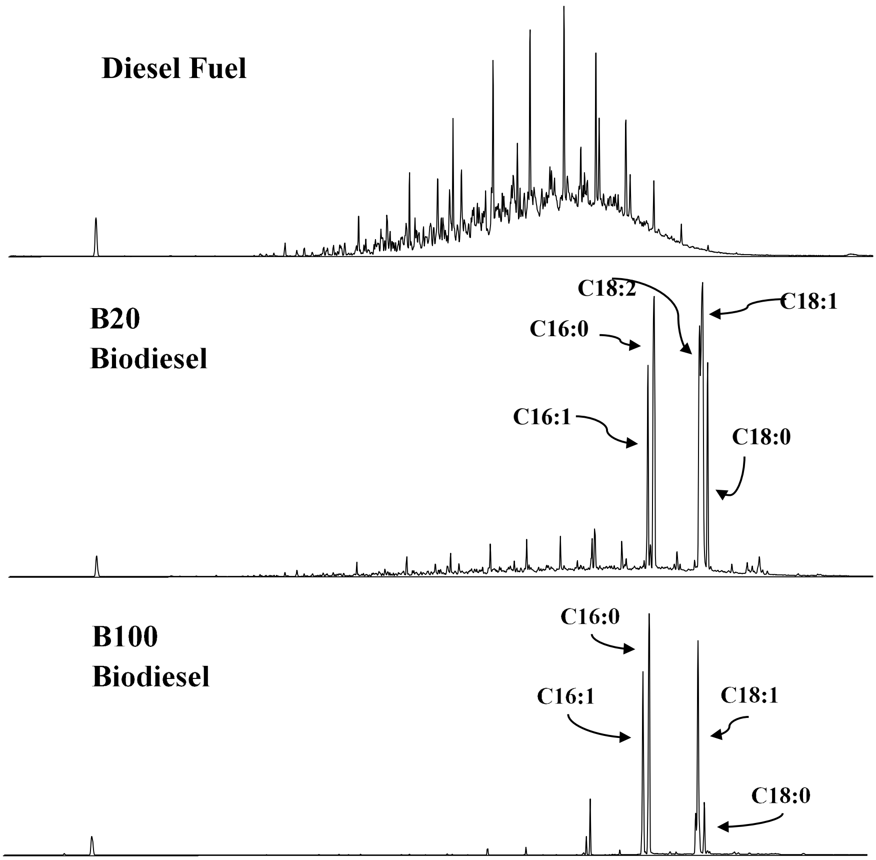


Fig. 4.10 TICs obtained using traditional fire debris methods. Solutions are 2% diluted in carbon disulfide. Top: diesel fuel. Middle: B20 biodiesel blend. Bottom: B100 biodiesel

Passive headspace concentration may not be an efficient extraction technique for the isolation of the FAMEs in biodiesel due to their somewhat low volatility [19]. As such, solvent extraction can be used on debris samples. Using the practice set forth in **ASTM E1386**, samples can be extracted after passive headspace concentration has occurred. Solvents, such as pentane or hexane, extract both petroleum-based products and FAMEs, allowing the identification of a biodiesel [19, 22].

Biodiesel may be identified using a traditional fire debris column or a specialized FAMEs column. Laboratories attempting to compare liquids, however, should use a polar column capable of baseline separation of FAMEs, such as those described in Sect. 4.2.6 [3, 10].

Like petroleum-based liquids, biodiesel is affected by **weathering**. The high boiling point of FAMEs makes the weathering of blended biodiesel products more difficult than a traditional heavy petroleum distillate. The higher the percentage of FAMEs present in the blend, the harder the liquid is to evaporate. As heat is

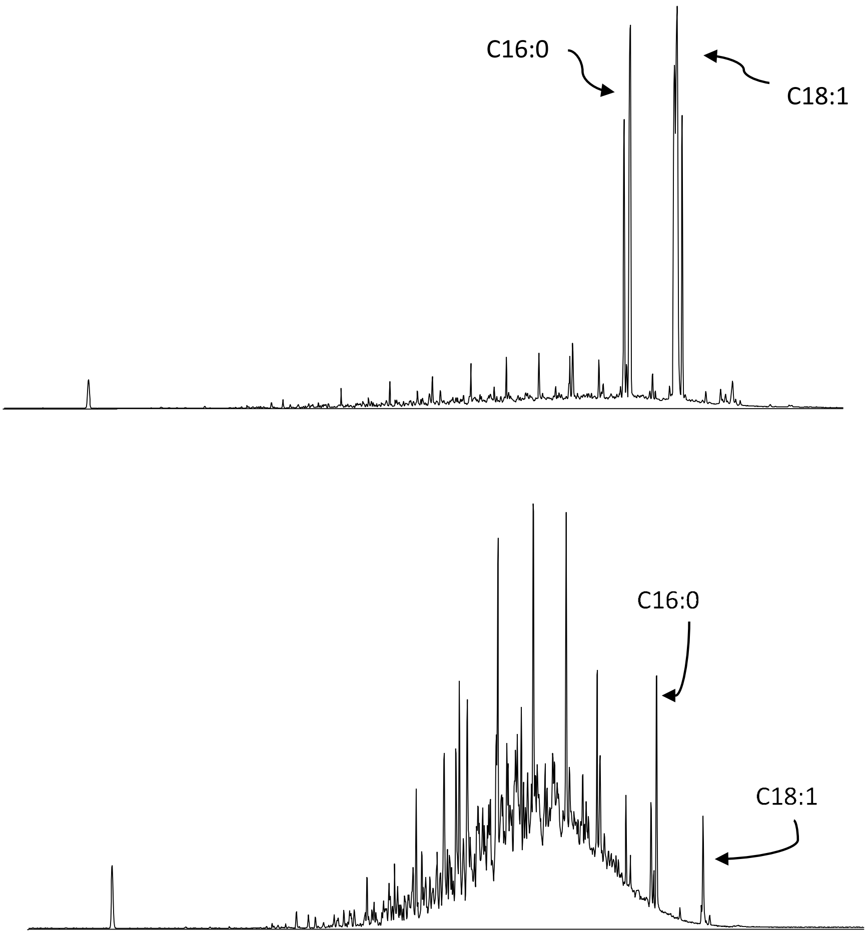


Fig. 4.11 TICs comparing liquid and headspace concentration of a B20 liquid. Top: 2% in carbon disulfide. Bottom: extract (passive headspace concentration for 16 h at 60 °C) obtained using a traditional ignitable liquid residue temperature program

applied, the distillate is reduced, and the FAMEs become more concentrated. As the sample is evaporated, the lighter end of the distillate is no longer visible, leaving a higher proportion of FAMEs. Eventually, the liquid turns into a dark resin-like liquid and will no longer evaporate. The overall composition of the FAMEs is not affected until the liquid is weathered over 75% [18].

Both thermal and metabolic oxidative decompositions can affect biodiesels (Fig. 4.12). While much is left to study about the effect microbes have on biofuels, it is clear they are subjected to degradation as other petroleum products are. In a blended fuel, the FAMEs are preferentially oxidized and can be undetectable within fourteen days [6, 18].

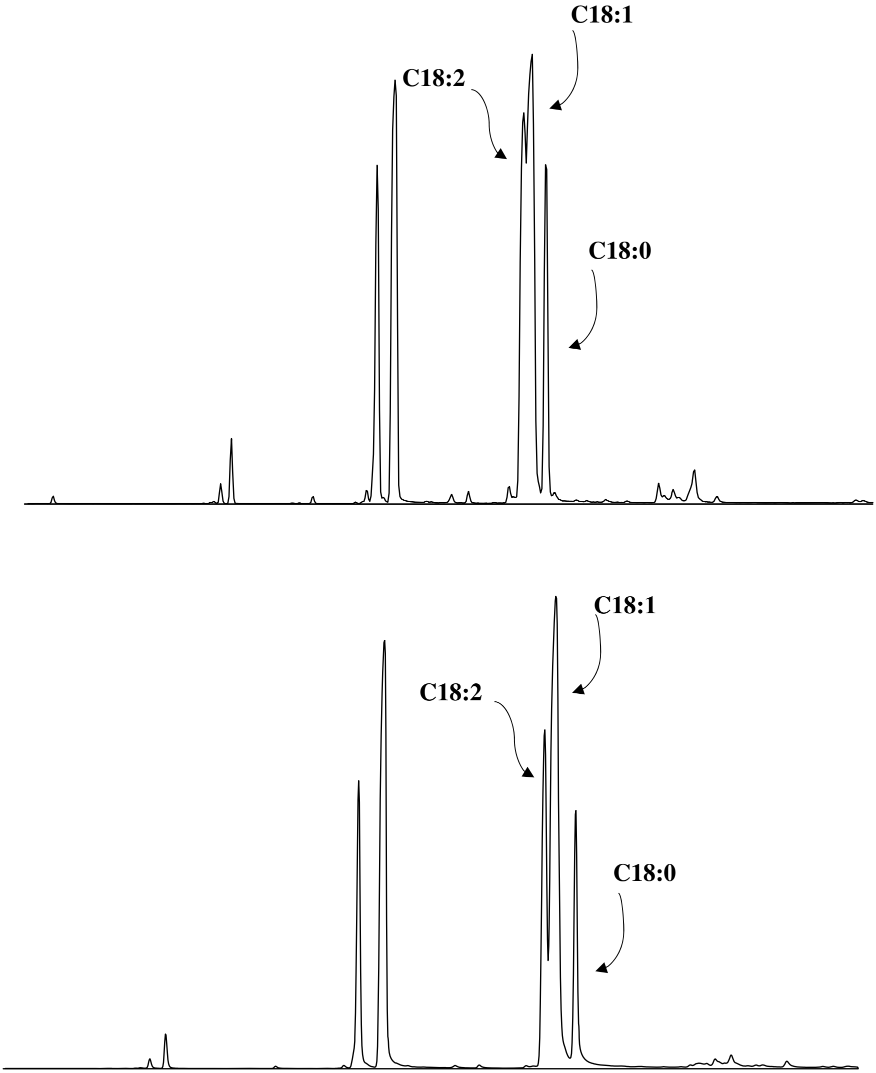


Fig. 4.12 Oxidation of FAs and FAMEs can occur over time and alter the overall composition of the sample. Image shows expanded chromatograms of fresh biodiesel (top) and biodiesel stored on a laboratory shelf in sealed glass vial (bottom). Peak 1 is C18:2, peak 2 is C18:1, and peak 3 is C18:0. Solutions are in carbon disulfide

4.3.3.1 Reporting

Recent changes to ASTM E1618 classify biodiesel as an oxygenated solvent [35]. While products which contain FAMEs as a major component can correctly be classified as an oxygenated product, low FAME blends, such as B5, only show the presence of FAMEs when they are highly evaporated, since the unevaporated liquid does not have a strong presence of oxygenated compounds [18]. EIC/EIPs should be used to screen heavy petroleum distillates for the presence of FAMEs in case of such a low FAME blend.

To aid investigators and other end users, laboratories may choose to report biodiesels using descriptors other than an oxygenated solvent. Identification of B100 can be written to include biodiesel (B100) as an example product. Blends containing diesel fuels can be reported as a mixture of a heavy petroleum distillate and a heavy oxygenated solvent, or FAMEs, to include biodiesel blended fuels.

4.3.4 Ethanol Fuel Refining and Fuel Blend Production

Ethanol is produced from starch or sugar-based feedstocks such as corn grain, sugarcane, sorghum, barley, sugar beets, and cellulosic feedstocks like wood chips and sawdust, as well as crop residues such as corn cobs and rice straw [27, 31]. Most of the feedstocks used in the USA to produce ethanol originate from corn grains [31]. Regardless of the feedstock used, the same chemical is produced.

To deter drinking, fuel ethanol produced in accordance with ASTM International standard methods is required to contain 1.76–5% denaturants. These can include natural gasoline, gasoline components, or unleaded gasoline. When gasoline products are used as the denaturant, the ability of the ethanol to absorb water is limited [26]. Once the ethanol meets ASTM International specifications, it is blended with gasoline products for distribution. At the time of blending, fuel ethanol must contain at least 92.1% ethanol and contain no more than 1% water [26].

Ethanol fuel is typically denoted by EXX, where XX is the percentage of ethanol in the fuel (Fig. 4.13). For example, E85 contains 85% ethanol and 15% gasoline. While all internal combustion engines can safely operate using E10 gasoline blends, only flex-fuel vehicles are rated for blends containing higher percentages of ethanol. Notices are placed on vehicles, so operators are aware the vehicle can use these blends. **Flex-fuel vehicles** are equipped with catalytic converters and fuel systems that are protected against the metal corrosion and deteriorating effects that high concentrations of ethanol can have on them [25]. In addition, the engine computer system adjusts the air/fuel ratio and the fuel injector is modified to compensate for the high ethanol concentrations.

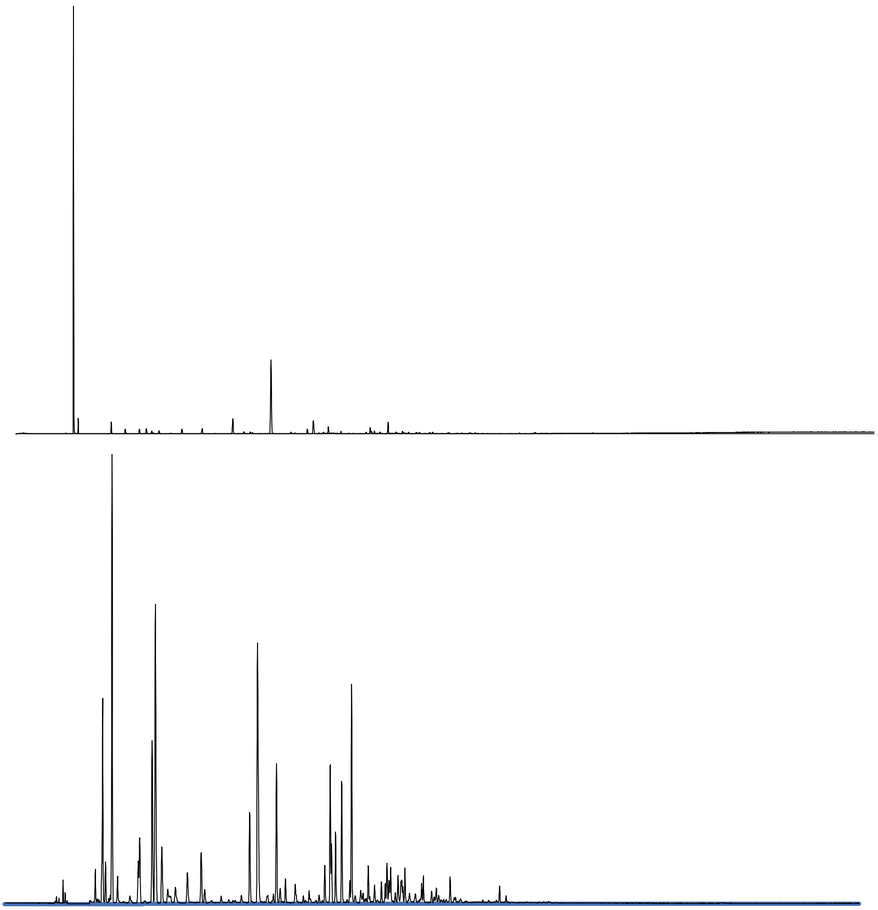


Fig. 4.13 Comparison of E85 and traditional gasoline. Top: 2% E85 in carbon disulfide. Bottom: 2% gasoline in carbon disulfide

4.3.5 Analytical Considerations, Data Interpretation, Classification, and Reporting of Ethanol-based Fuels

Laboratories can receive samples in either liquid or debris form. Liquid samples can be analyzed in the same way as other ignitable liquids, as covered in Chap. 2. Unlike vegetable oils, E85 gasolines are not prone to storage issues, as can be seen in Fig. 4.14. Even with weathered samples, ethanol remains the dominant peak until the liquid is highly evaporated ($\sim$98%) [19].

Condensation and fuel temperature fluctuations can cause water to absorb into the fuel. Once enough water has absorbed to reach the saturation level of the fuel, the water and alcohol separate away from the remaining fuel and form a bilayer

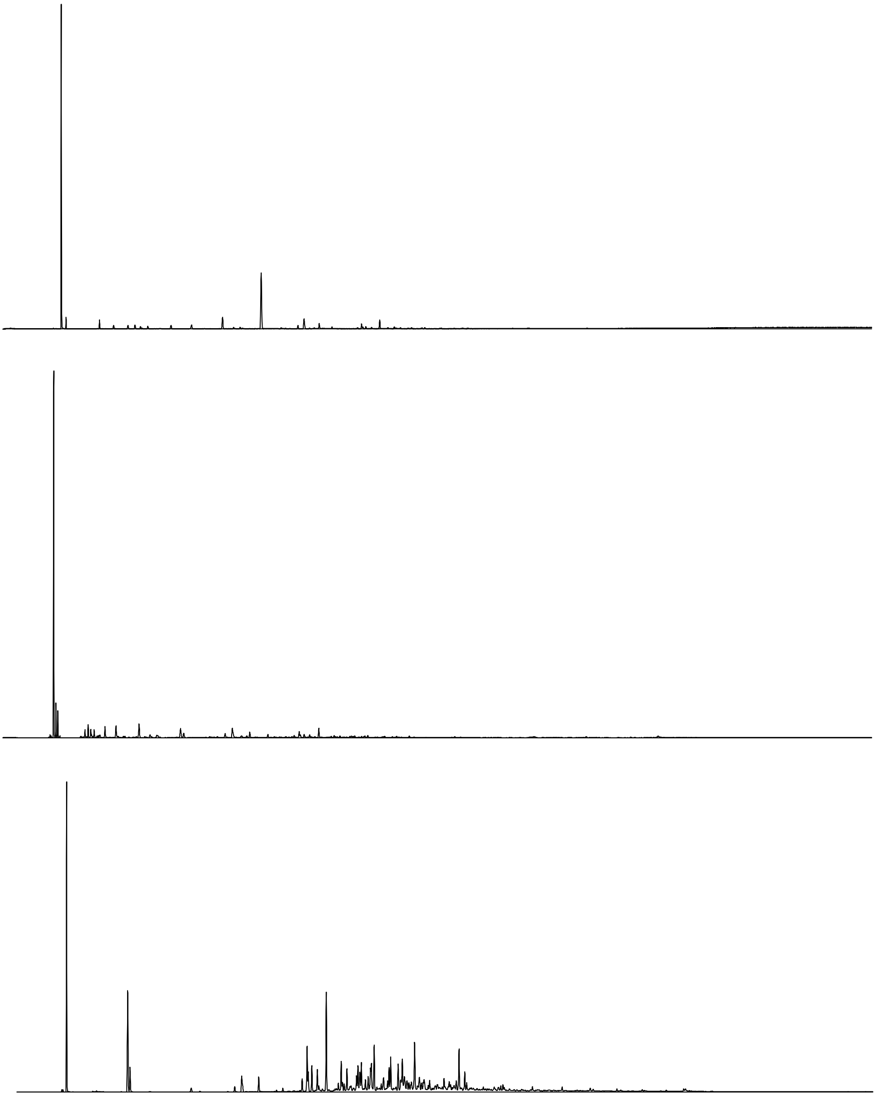


Fig. 4.14 Top: E85 liquid reference sample obtained in 2007 and analyzed in 2011, with a dominant ethanol peak. Middle: the same E85 sample analyzed in 2018. Note the stability of the ethanol during storage. Bottom: 98% evaporated E85 gasoline, where the TIC begins to show a characteristic gasoline pattern

(Fig. 4.15) [36]. If the liquid has formed a bilayer, either from absorption of water or from separation of denaturants, it is important to identify both the ethanol and the gasoline in the sample. Ethanol, while present in both layers, will be dominant in the aqueous fraction, while the gasoline will be identifiable in the organic layer. These can be separated via liquid–liquid extraction for further analysis.

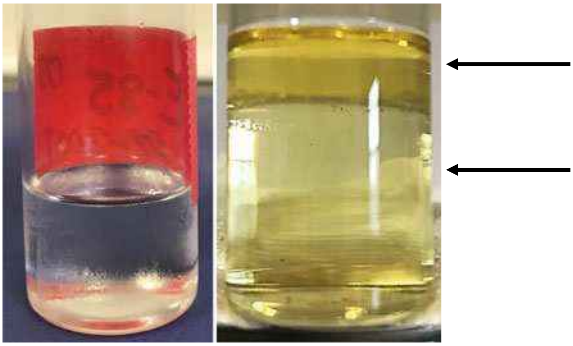


Fig. 4.15 Left: E85 liquid reference sample. Right: E85 recovered from a vehicle fuel tank showing ethanol separating to form a bilayer

Characterization of the organic layer is important when laboratories attempt to identify possible sources of engine failure. When an incompatible fuel is used in an engine, excessive wear can occur due to oxidation and degradation of the engine components [37]. This type of damage has been seen in insurance fraud cases involving incorrect fuels being used in vehicles. If a representative sample is collected from the vehicle, it can be tested for the presence of incorrect fuel types, contaminants and additives, oxidation and degradation by-products can be identified, and particulates are noted.

Since **passive headspace concentration** can extract both the ethanol and the gasoline from the headspace, ethanol-based fuels can be recovered with this technique, given the proper GC-MS program. While the ethanol is still dominant, the gasoline fraction can be more pronounced due to displacement of the ethanol by gasoline compounds [19]. Some GC-MS methods begin collecting data after the solvent has passed the detector, a period commonly referred to as a **solvent delay**. Methods which have a solvent delay that extends after the elution solvent has passed the detector risk missing the ethanol fraction, depending on the solvent choice. Having earlier retention times than most solvents, the ethanol may not appear, and examiners may only observe gasoline (Fig. 4.16) [19].

As discussed in Chap. 2, the GC-MS method can be adjusted so that the detector is on right after injection and then turns off during the elution of the solvent, as in the bottom of Fig. 4.16. The molecular weight of ethanol is 46 amu, and many of the diagnostic ions are less than 40 amu. As such, the scan range of the mass spectrometer should also be adjusted to have a lower starting *m/z* of 15 [19].

Due to the low abundance of gasoline in E85, the TIC may not show obvious signs of gasoline; extracted ion profiles/chromatograms, however, will show characteristic gasoline patterns (Fig. 4.17).

The increasing use of ethanol in gasolines makes it more difficult to determine if a debris sample contains E85. Laboratories who wish to report a sample as an ethanol-based fuel should exercise caution, as all standard gasolines could contain up to 10% ethanol. A large abundance of ethanol relative to the gasoline pattern should be present if E85 reporting is considered. Even though ethanol is dominant in the sample, ASTM E1618 classifies ethanol-blended fuels as gasoline [35].

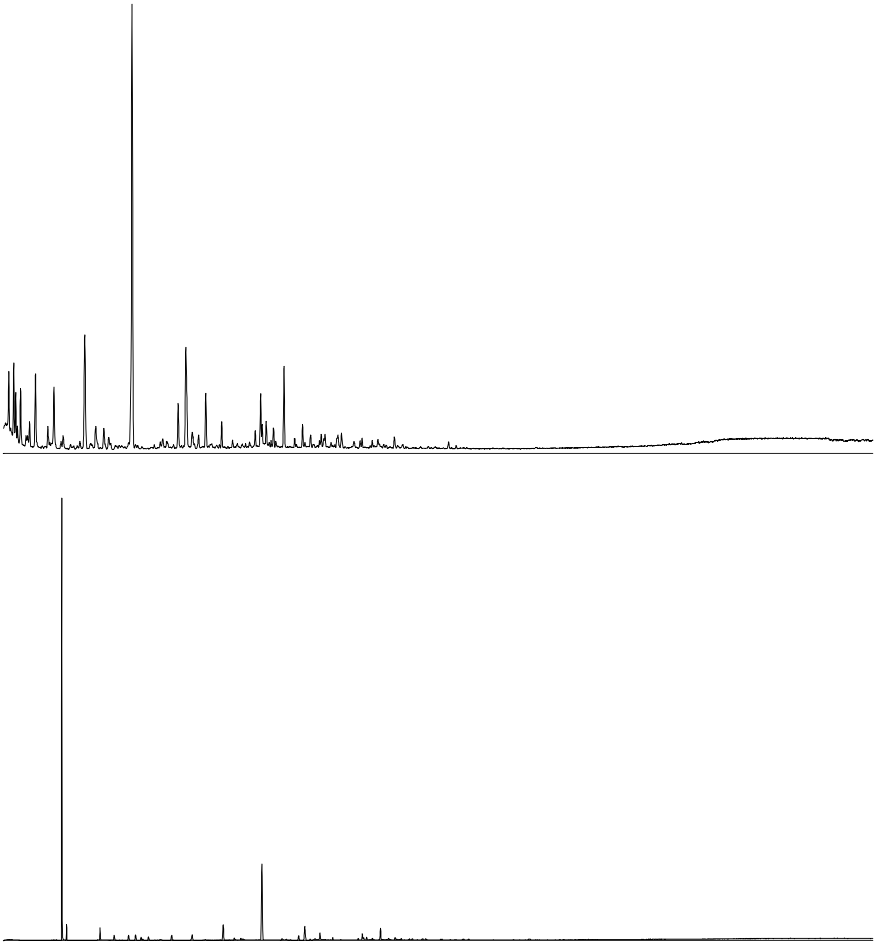


Fig. 4.16 Top: E85 liquid reference sample analyzed using a solvent delay. Bottom: same E85 gasoline analyzed without the solvent delay

As with the biodiesel blends, the examiner may choose to report ethanol-blended fuels as a mixture of ethanol and gasoline. While the examiner may not be able to state unequivocally that the fuel is an ethanol-blended fuel, these fuels can be mentioned as an example of such a mixture. Examiners must also consider the containers or matrix which the sample was obtained from. If the liquid sample or debris is from the bottle of an alcoholic beverage, it is possible that the beverage is the source of the ethanol.

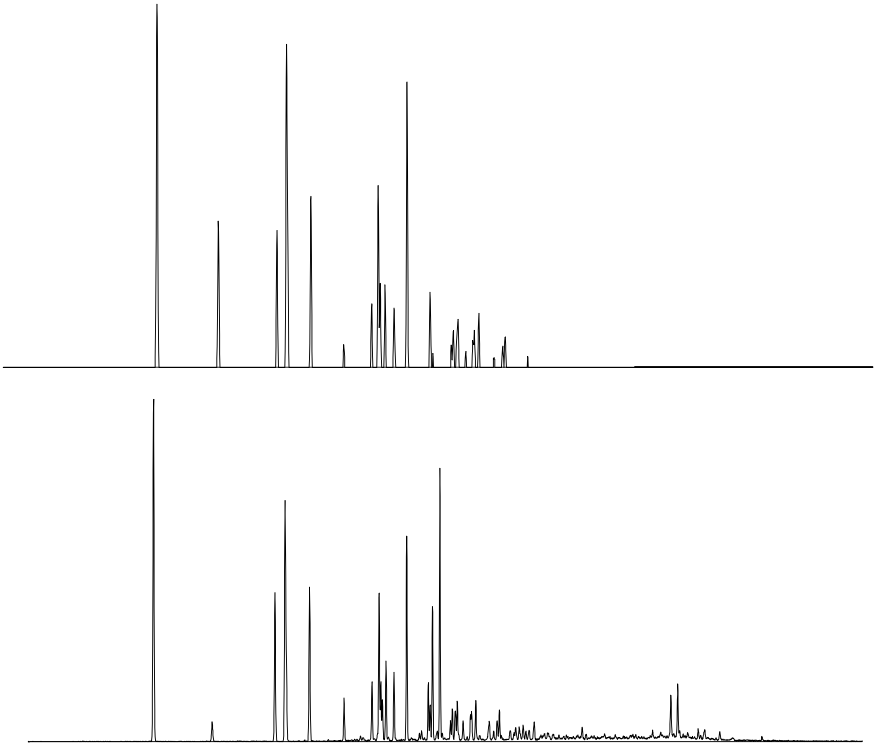


Fig. 4.17 Top: aromatic profile of an E85 liquid reference sample. Bottom: Matrix sample was burned and then spiked with 20 μL of E85. Data shows the aromatic profile from 16 h of passive headspace concentration at 60 °C

4.4 Future Needs and Challenges

The understanding of vegetable oils, spontaneous ignition, and alternative fuels by the fire debris community has increased in recent years; however, much is still left to study. Well-constructed studies are needed to better understand the changes that result from storage conditions, how FAs change when weathered or subjected to fire conditions and subsequent extinguishment, and the effects of incomplete combustion as well as microbial degradation [10, 14, 38]. This information can provide best practices for storage conditions of liquid and debris samples, extracted samples, and understanding of how to handle samples where multiple types of analyses are requested.

Equally important is an understanding of the materials which contain VOR, FAs, and FAMEs. Laboratories and analysts are encouraged to maintain **reference liquids** and **matrix samples** for testing. If a strong peak or pattern is present that is not normally seen in traditional petroleum products, examiner should take caution and consider screening the sample for an alternative fuel or VOR.

It is imperative that fire debris examiners remain cognizant of changes in both the fuel markets and the new technologies. As manufacturers find additional uses for VORs and create new alternative fuels and new technologies to produce them, it will become more important for examiners to keep abreast of the changes. New "**green**" **products**, such as lighter fluids and torch fuels, are making their way to the market and into fire debris samples. These products not only challenge our understanding of what is considered an ignitable liquid product but how to properly extract, analyze, and classify them. A firm understanding of the patterns of petroleum products as well as alternative fuels can help prevent misidentifications.

Striving to look not only at the information geared toward fire debris examiners, but all avenues of VOR and alternative fuel research, can help the field stay current.

4.5 Questions

1. True or False: All triglycerides, whether they originate from plants or animals, are considered vegetable oils.
2. Can all vegetable oils undergo oxidative polymerization to form hard films?
3. Are autoignition and spontaneous ignition interchangeable terms?
4. Is passive headspace an acceptable recovery technique for FAs? How about biodiesel? Why or why not?
5. What is the most common method for creating FAMEs?
6. What feedstocks are used to create biodiesel?
7. Can the ethanol in E85 fuels be detected on GC-MS methods that use a solvent delay?

References

1. Tyson S (2001) Biodiesel handling and use guidelines
2. Stauffer E (2005) A review of the analysis of vegetable oil residues from fire debris samples: spontaneous ignition, vegetable oils, and the forensic approach. J Forensic Sci 50:1–10
3. Stauffer E, Dolan JA, Newman R (2007) Fire debris analysis. Academic Press, Cambridge
4. Pitts SJ, Thomson CI (2003) Analysis and classification of common vegetable oils. J Forensic Sci 49:1147
5. Stauffer E (2005) A review of the analysis of vegetable oil residues from fire debris samples: spontaneous ignition, vegetable oils, and the forensic approach. J Forensic Sci 50:1–10
6. Schwenk LM, Reardon MR (2009) Practical aspects of analyzing vegetable oils in fire debris. J Forensic Sci 54:874–880. https://doi.org/10.1111/j.1556-4029.2009.01067.x
7. Morrison, D, Su YS, Fecke MJ (2006) Spontaneous combustion tendency of household chemicals and clothes dryers: part 1. Appliance Magazine 63(6):36–41
8. Knörr W, Daute P, Grützmacher R, Höfer R (1995) Development of new fields of application for linseed oil. Fett Wissenschaft Technologie/Fat Sci Technol 97:165–169. https://doi.org/10.1002/lipi.19950970502

9. Babrauskas V (2003) Ignition handbook: principles and applications to fire safety engineering, fire investigation, risk management and forensic science. Fire Science Publishers, Issaquah
10. Stauffer E (2006) A review of the analysis of vegetable oil residues from fire debris samples: analytical scheme, interpretation of the results, and future needs. J Forensic Sci 51:1016–1032. https://doi.org/10.1111/j.1556-4029.2006.00220.x
11. Byron D (2005) Analysis of vegetable oil residues from fire debris samples. Presented for the Metro Fire Investigators Association, Atlanta, GA, 15 June 2005
12. De Haan, JD (1996) Spontaneous ignition, part I: what really happens. Fire Arson Invest 46:13–17
13. De Haan JD (1996) Spontaneous ignition, part II: investigation. Fire Arson Invest 46:8–11
14. Gambrel AK, Reardon MR (2008) Extraction, derivatization, and analysis of vegetable oils from fire debris. J Forensic Sci 53:1372–1380. https://doi.org/10.1111/j.1556-4029.2008.00882.x
15. Gunstone FD, Hilditch TP (1945) The union of gaseous oxygen with methyl oleate, linoleate, and linelenate. J Chem Soc 836–841
16. Rampling K (2000) Spontaneous combustion of drying oils as a fire cause. T.C. Forensic, Lansvale
17. DeHaan JD (2002) Kirk's fire investigation, 5th edn. Prentice Hall, Upper Saddle River
18. Goodman MR, Kaley EA, Finney EE (2016) Forensic analysis of biodiesel. Forensic Sci Int 263:10–26
19. Kuk RJ, Spagnola MV (2008) Extraction of alternative fuels from fire debris samples. J Forensic Sci 53:1123–1129. https://doi.org/10.1111/j.1556-4029.2008.00823.x
20. ASTM E1412-16 (2016) Standard practice for separation of ignitable liquid residues from fire debris samples by passive headspace concentration with activated charcoal. ASTM International, West Conshohocken, PA, www.astm.org
21. ASTM E1386-15 (2016) Committee practice for separation of ignitable liquid residues from fire debris samples by solvent extraction. ASTM International, West Conshohocken, PA, www.astm.org
22. ASTM 2881-18 (2016) Committee test method for extraction and derivatization of vegetable oils and fats from fire debris and liquid samples with analysis by gas chromatography-mass spectrometry. ASTM International, West Conshohocken, PA, www.astm.org
23. A beginner's guide to mass spectrometry of fatty acids: part 1. Methyl esters. http://www.lipidhome.co.uk/ms/basics/ms-begin-1/index.htm. Accessed 2 Nov 2018
24. Gerpen JV (2005) Biodiesel processing and production. Fuel Process Technol 86:1097–1107. https://doi.org/10.1016/j.fuproc.2004.11.005
25. Duffield JA, Johansson R, Meyer SUS. Ethanol: an examination of policy, production, use, distribution, and market interactions. 87
26. Weaver JW, Skaggs SA, Spidle DL, Stone GC. Composition and behavior of fuel ethanol. 69
27. Biofuels: ethanol and biodiesel—energy explained, your guide to understanding energy. Energy Information Administration. https://www.eia.gov/energyexplained/index.php?page=biofuel_home. Accessed 2 Nov 2018
28. Stauffer E, Byron D (2007) Alternative fuels in fire debris analysis: biodiesel basics. J Forensic Sci 52:371–379. https://doi.org/10.1111/j.1556-4029.2006.00380.x
29. Lipid Technology Newsletter (1998) US legislates for increased biodiesel use. Lipid Technology Newsletter, August 1998, vol 4, No 4, p 73
30. ASTMD6584-17 (2016) Standard test method for determination of total monoglyceride, total diglyceride, total triglyceride, and free and total glycerin in B-100 biodiesel methyl esters by gas chromatography. ASTM International, West Conshohocken, PA, www.astm.org
31. Alternative Fuels Data Center. Ethanol fuel basics. https://www.afdc.energy.gov/fuels/ethanol_fuel_basics.html. Accessed 2 Nov 2018
32. Haas M (2004) The interplay between feedstock quality and esterification technology in biodiesel production. Lipid Technol 16:7–11

33. Ejikeme PM, Anyaogu ID, Ejikeme CL, Nwafor NP, Egbuonu CAC, Ukogu K, Ibemesi JA (2010) Catalysis in biodiesel production by transesterification process—an insight. E-J Chem 7(4):1102–1132
34. Newman RT, Dietz WR, Lothridge K (1996) The use of activated charcoal strips for fire debris extractions by passive diffusion. Part 1: the effects of time, temperature, strip size, and sample concentration. J Forensic Sci 41:361–370. https://doi.org/10.1520/JFS13922J
35. ASTM E1618-14 (2014) Standard test method for identification of ignitable liquid residues in extracts from fire debris samples by gas chromatography–mass spectrometry. ASTM International, West Conshohocken, PA, www.astm.org
36. Allen M (2010) Can ethanol damage your engine? Yup. Here’s how. In: Popular mechanics. https://www.popularmechanics.com/cars/alternative-fuel/biofuels/e15-gasoline-damage-engine. Accessed 2 Nov 2018
37. Stauffer E, Bonfanti M (2006) Forensic investigation of stolen-recovered and other crime-related vehicles. Elsevier, Amsterdam
38. Hanger C, Runkle D (2017) Forensic science assessments: a quality and gap analysis. Fire investigation, a plain language summary. AAAS

Douglas Byron is the President of Forensic and Scientific Testing, Inc., an accredited independent laboratory system which specializes in fire debris analysis. For over 25 years, he has performed examinations on fire debris evidence, presented at various meetings, and authored publications on fire debris analysis with an emphasis in fatty acids, spontaneous combustion and alternative fuels.

Chapter 5
Variation Within Ignitable Liquid Classes

Mary R. Williams and Susan Seebode Hetzel

Learning Objectives

- Understand there is variation within ASTM E1618 classes
- Understand the types of some of the observed variation
- Understand some variation is due to differences in carbon range of compounds
- Understand the petroleum refining process, distribution, and product filling practices may be a source of observed variation.

5.1 Introduction

Chapter 2 discussed the typical characteristics of ignitable liquid classes and gave examples of their "classic" presentations. The major focus of this chapter will be on the variability observed within the various classes of refined petroleum products. The variability seen in the oxygenated and miscellaneous classes does not follow an established pattern. As such, examples of each will be discussed, but the examiner must always consider that they have the potential to be endlessly variable.

The variability in refined petroleum products starts with the characteristics and variability of the petroleum feedstocks used in the refinery process. The feedstocks used contain both aliphatic and aromatic components; however, the composition can be varied. Figure 5.1a and b shows the TIC and common EIPs used in the interpretation of fire debris samples for two different raw petroleum feedstocks. The Pennsylvania crude oil (Fig. 5.1a) is comprised mostly of normal alkanes, cycloalkanes, and branched alkanes, with no major peaks consistent with alkenes

---

M. R. Williams
National Center for Forensic Science, University of Central Florida, Orlando, FL, USA

S. S. Hetzel (✉)
S-E-A Ltd, Columbus, OH, USA

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_5

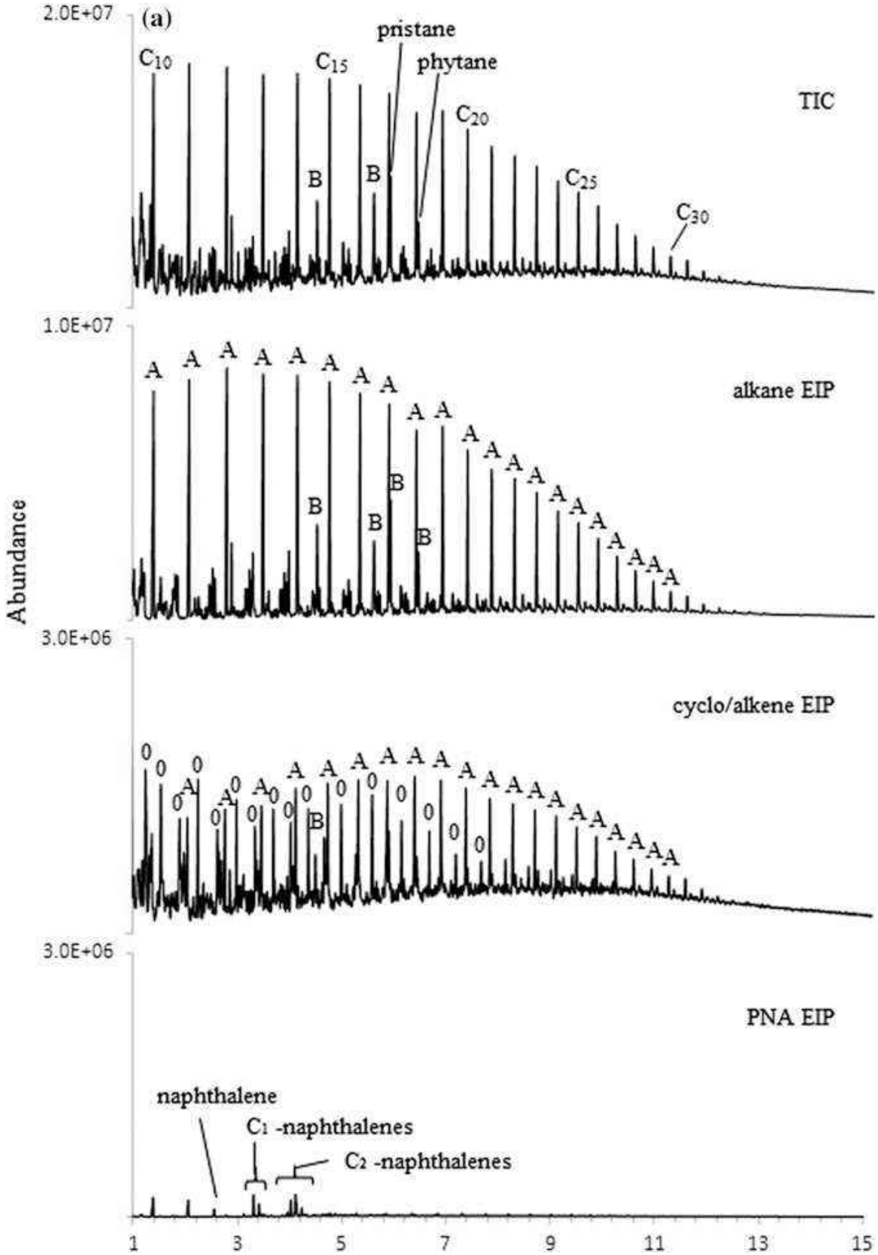


Fig. 5.1 a TIC and EIPs of Pennsylvania crude oil; no data was collected for any components eluting prior to C_3-alkylbenzenes. Peaks denoted with an "A" are normal alkanes, with "0" are tentatively identified as cycloalkanes, and with a "B" are tentatively identified as branched alkanes. **b TIC and EIPs of shale oil**, NIST SRM#1580; no data was collected for any components eluting prior to C_3-alkylbenzenes. Peaks denoted with an "A" are normal alkanes, with an "E" are tentatively identified as alkenes, with "0" are tentatively identified as cycloalkanes, and with a "B" are tentatively identified as branched alkanes

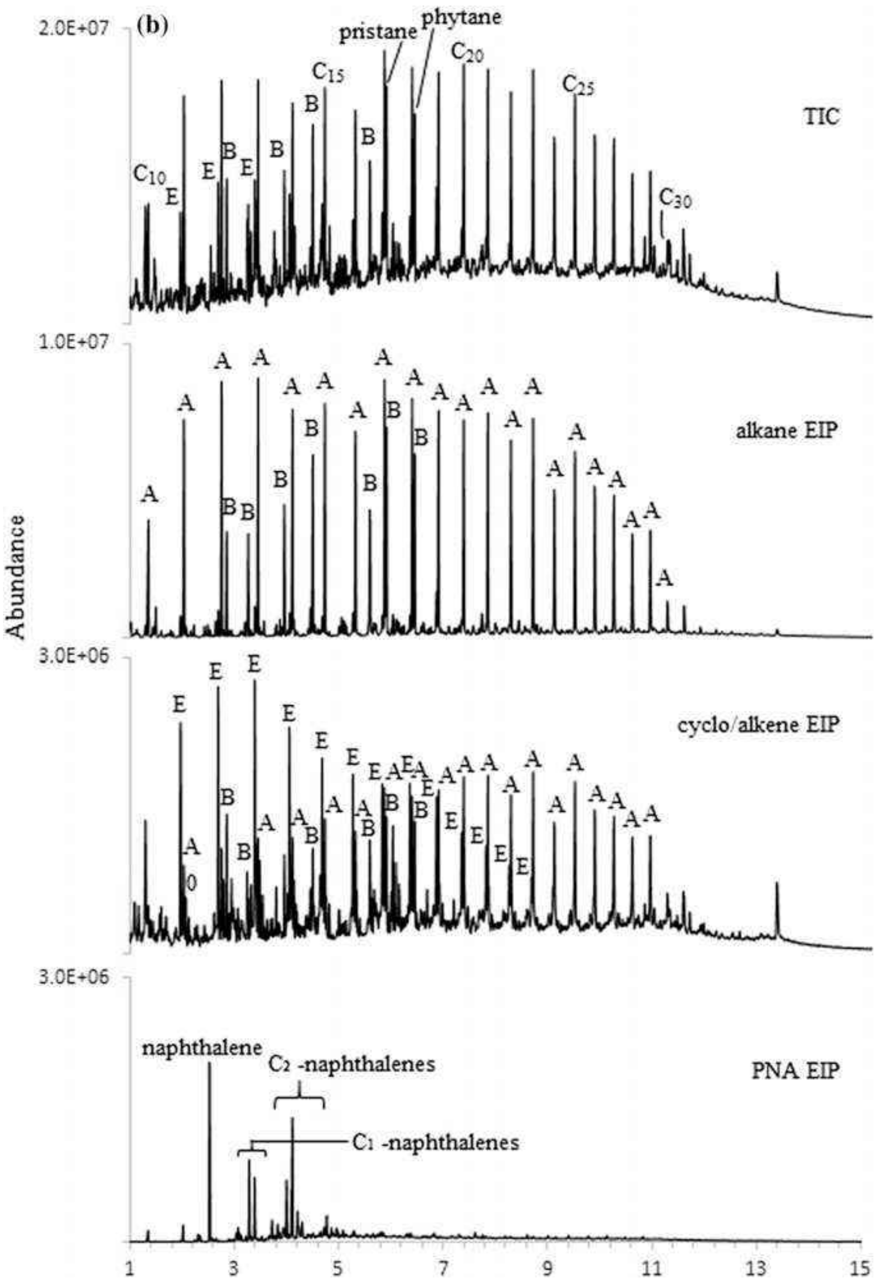


Fig. 5.1 (continued)

and almost no PNAs present. Conversely, the shale oil reference sample (Fig. 5.1b) is comprised mostly of normal alkanes, alkenes, and branched hydrocarbons, with little cycloalkanes and significantly more initial PNA response. While both have normal alkanes as the most abundant compound class, there are clear differences in the overall composition.

Typically, the refining process of crude oil involves distillation, catalytic (cat) cracking, alkylation, isomerization, and reforming, which produces a variety of product streams (see Chap. 2). Some of the refinery initial product streams are sold directly to manufacturers and distributors, but most are further refined or blended with one another to generate products that meet specific customer requirements.

Unless the final product is a low-volume specialty product, the refined product is commonly transported by underground pipeline (in the USA [1]) to an oil depot (sometimes also called a tank farm or oil terminal). Multiple refineries may contribute to the stock held by a single oil depot, often in the same tank, which creates a mixture. The crude oil source, pipeline distribution system, and the comingling of "like" products at the oil depot, all produce variability.

Product specifications are another source of variability. There are many industry-wide **specifications** for the production of various products that are considered by fire debris examiners to be ignitable liquids. Table 5.1 lists a small sampling of consensus specifications that have been developed through ASTM. A distribution company or retailer will additionally have a **specification sheet** that details the characteristics required for a particular product (e.g., color, flash point, viscosity, corrosivity, odor, required physical properties). Some of these characteristics can be altered by adjusting the chemical composition of the product, such as reducing the aromatic content to manufacture a product that generates less soot upon burning. Other considerations that may also be included in an individual

Table 5.1 Examples of some ASTM industry standard specifications that might relate to ignitable liquids encountered in fire debris analysis

ASTM*	Describes specifications for:
D4814	Spark-ignition engine fuel (gasoline)
D235	"Mineral spirits" in the coatings (e.g., paint) and dry-cleaning industries
D396	Various types of fuel oils, including No. 1 fuel oil (e.g., kerosene) and No. 2 fuel oil (e.g., diesel or home heating oil), as well as fuel oil numbers 4, 5, and 6
D975	Diesel fuels
E3050	Denatured ethanol used for cooking or appliance fuel
D4806	Ethanol-based fuels blended with gasoline for spark-ignition engines (e.g., E85, ethanol denatured with gasoline)
D7467	Biodiesel fuel oil blends from B6 to B20
D1152	Methanol used as solvents, plasticizers, and chemical intermediates
D3735	"VM&P naphthas" primarily used in the coating industry

* All ASTM standards referenced are published by ASTM International and can be found at https://www.astm.org

specification sheet could relate to possible health effects, safety, and local (e.g., Californian) regulations.

Some product specification sheets are very exacting, while others are more general in nature. For instance, a more general specification for a product to be marketed as a charcoal lighter fluid could be one that requires the material to be a petroleum product that has a flash point above a specific temperature [e.g., above 38 °C (100 °F)], with no other limitations on chemical content. This specification sheet could be satisfied by numerous different petroleum products, including most medium- and all heavy-range products, and could be any of the following ASTM E1618-14 classifications: petroleum distillate (with or without aromatic content), isoparaffinic product, naphthenic–paraffinic product, normal alkane product, aromatic product, or a blend of two or more of those listed above. When the distributor or retailer sells out of their first delivery of the product, the next shipment of the product, potentially sold with identical labeling other than the manufacturing lot/batch number, may have completely different chemical content, while still meeting all the requirements of the particular product's specification sheet. This imparts the possibility of wide variability to even identically labeled consumer products.

In general, the **variation** observed in petroleum products is related to the carbon range and the ratio of the various chemical classes (i.e., normal alkanes, aromatic content, and branched alkanes) to one another. Because the carbon range is so important in addressing variability, many chromatograms throughout this chapter have carbon numbers labeled. For example, the label "C_8" or "8" on a chromatogram indicates the retention time for n-octane. Additionally, in the figures, the notations of alkyl-substituted aromatic compounds have been shortened by removing the word "alkyl" (e.g., C_2-benzenes instead of C_2-alkylbenzenes) for brevity.

5.2 Gasoline

Although we may think of **gasoline** as a simple commodity, in actuality it is a complex mixture of various petroleum refinery streams and other performance or regulatory additives that are all blended together. In the USA, gasoline (except when an oxygenate is the primary component, such as in E85) must meet the requirements of ASTM D4814, Standard Specification for Automotive Spark-Ignition Engine Fuel [2]; in the European Union, petrol (gasoline) must meet the requirements of EN 228 [3]. Some of the requirements or specifications for gasoline within ASTM D4814 include: octane, vapor pressure (which affects ease of starting when hot or cold, drivability, and has a large effect on air quality), vapor–liquid ratio, distillation characteristics, sulfur content, and oxygenate content, to name a few.

To meet the requirements of ASTM D4814, gasoline may have to have different characteristics from month to month, or even county to county. The *chemical* content of gasoline is not constant or strictly defined by ASTM D4814, while the *characteristics* of gasoline are defined. The refinery will have a variety of materials readily available for blending that will not be constant. Therefore, the composition of the gasoline being blended at each refinery would be expected to change over time. Many of the requirements of ASTM D4814 must be fulfilled by the actions of the refinery when blending their product streams; only some can be addressed further downstream in the distribution chain. Further, the composition of the gasoline must change in response to the needs of the end consumer. Gasoline in summer months or warmer climates will look slightly different than those in winter months or colder climates to account for changes in vapor pressure due to season or climate. For example, a warm weather blend might not produce enough vapor to efficiently start an engine in an Alaskan winter.

The requirements of modern engines cannot be met by petroleum processing alone, so a range of additives are included in order to facilitate specific properties or characteristics. Some of these additives are included at the refinery, while some are in the additive package included in the final delivery tanker truck that goes to the retail station. Additive packages are formulated so that the final gasoline at the retail site will meet the requirements of ASTM D4814, and may also be based on brand (which may include the use of proprietary components such as detergents, octane boosters, or stabilizers). For instance, any required ethanol (or other oxygenate) is added when the tanker truck is filled at the oil depot, because ethanol and other light oxygenates cannot be transported through the current underground pipeline system [4]. With changes in characteristics over time and location based on regulation requirements, the blending of product streams at the refinery to meet characteristic requirements, transportation through shared pipelines, and the mixing of multiple batches of product at the oil depot, variability in the composition of gasoline samples should be expected.

In the analysis of fire debris samples, the criteria for the identification of gasoline according to ASTM E1618-14 [5] require an aromatic pattern comparable to a reference and an associated alkane pattern. The general range of variability found in gasoline will be discussed. All the gasolines chromatographically presented here were included in a set of 71 gasolines that were evaluated in a survey of US gasolines [6].

5.2.1 Variability in the Alkane-to-Aromatic EIP Ratio

Gasoline contains aliphatic and aromatic hydrocarbon content; the relative concentration of each of these hydrocarbon classes is a type of variation among gasolines. This difference is reflected in the ratio of the alkane and aromatic extracted ion profiles (EIPs). In the examples of gasoline presented here, relative ratios were obtained by comparing the approximate maximum abundance (maximum peak height) for each profile. Based on the 71 samples of gasoline that were compared [6], the average, highest, and lowest alkane-to-aromatic ratios observed at

Table 5.2 Approximate ratios of the alkane to aromatic EIP of gasoline at various levels of evaporation

Level of evaporation	Alkane: aromatic EIP ratio		
	Average	Low	High
Neat/unevaporated	1:1	1:6	6:1
50% evaporated	1:2	1:12	3:1
90% evaporated	1:8	1:20	1:2

three levels of evaporation (also referred to as weathering) are presented in Table 5.2.

The aromatic EIP is typically the dominant pattern for gasoline, at all evaporation levels, except the highly evaporated samples (greater than 95%). As most of the aliphatic response comprises the more volatile components of gasoline (eluting before C_8), the alkane EIP can dominate in neat samples of gasoline. Note that an average ratio of 1:1 for unevaporated gasoline listed in Table 5.2 can be somewhat misleading. It only takes the concentration of one aliphatic hydrocarbon to approach that of toluene for the ratio to be 1:1. Typically, when the alkane EIP pattern does dominate over the aromatic EIP, it is due to the concentration of 2,2,4-trimethylpentane (isooctane).

Weathering of a petroleum product occurs when it is exposed to heat and/or time, causing the most volatile components to be lost by evaporation. As the liquid is weathered, the most volatile components are lost, and the overall ignitable liquid pattern shifts. The early eluting components' relative concentration will decrease, while the later eluting components' relative concentration will increase. This is demonstrated in Table 5.2 with the change in the average alkane-to-aromatic ratio based on the level of evaporation of gasoline. Most of the alkane content of gasoline elutes prior to octane and thus is lost through evaporation more quickly than the later eluting aromatic content. As such, the alkane content relative to the aromatic content will decrease with increasing evaporation. When gasoline is highly evaporated to the point where the aromatic content is lost (see Sect. 5.2.6), heavy alkane content may be visible that was not previously observed.

5.2.2 Aromatic EIP Variability

When looking only at the response from gasoline samples, the aromatic pattern is relatively consistent. Reformate is the refinery stream most commonly used as the source for the aromatic content of gasoline. Even when the alkane EIP content dominates in abundance, a broad range of aromatic content is generally visible in the TIC. Occasionally, samples with slightly different inter-group ratios are encountered. Figure 5.2a, b depicts the aromatic response for "typical" unevaporated and evaporated gasoline (chromatogram a), as compared to one with low C_2-alkylbenzene response (chromatogram b) and one with high toluene response (chromatogram c). As discussed in Chap. 3, interpreting the aromatic pattern is

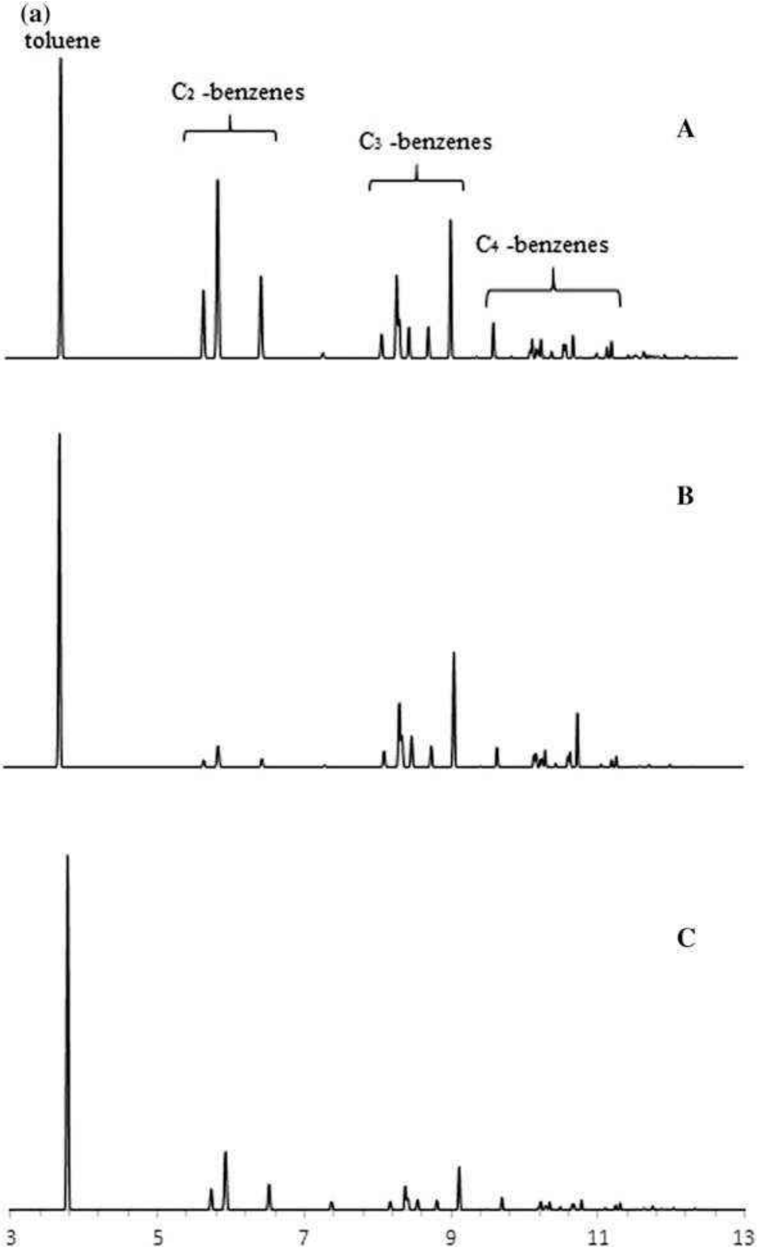


Fig. 5.2 **a** Comparison of the aromatic EIPs of neat gasolines from Florida (A, 87-octane, and B, 93-octane) and from Ohio (C, 93-octane). **b** Comparison of the aromatic EIPs of the same gasolines shown in **a**, after they were evaporated 90% by volume (weathered)

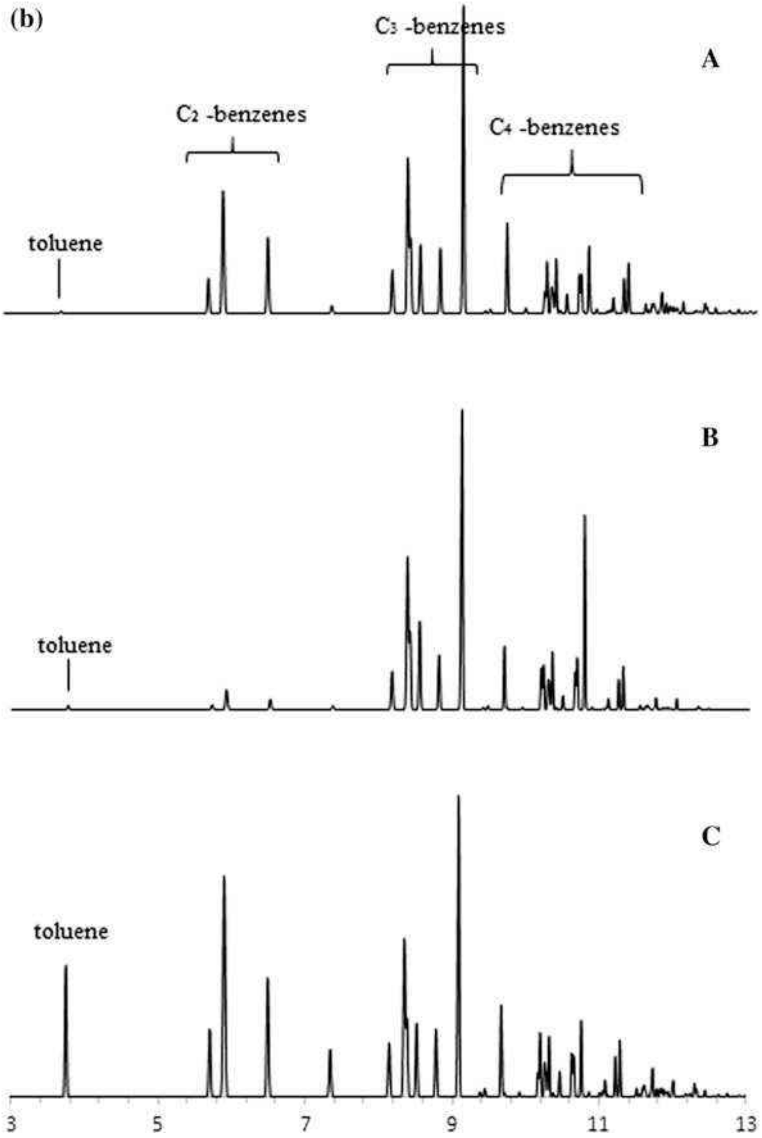


Fig. 5.2 (continued)

significantly more difficult when the response from the matrix of the fire debris is also present in the chromatogram.

The evaporative loss an ignitable liquid undergoes as it weathers is typically visible in the TIC and EIPs. In comparing Fig. 5.2a and b, the chromatographic effect of weathering is evident. The most volatile components of the aromatic EIP, toluene and the C_2-alkylbenzenes, decrease as the relative abundance of the C_3-alkylbenzenes increases. As such, there is an overall shift of the pattern toward the heavier side of the profile. This illustrates the variable appearance of a single ignitable liquid due to evaporation. However, it should be noted that with evaporative loss, the intragroup ratios (i.e., the ratio of peaks within the C_2-alkylbenzenes or within the C_3-alkylbenzenes) of components remain largely consistent.

5.2.3 Alkane EIP Variability

The alkane pattern of gasoline is highly variable. The majority of the alkane EIP content in gasoline elutes early in the chromatogram (before C_8) to improve the ability of the fuel to start a cold engine. The alkane EIP pattern is typically the second most abundant pattern in neat and lightly (up to 50%) evaporated samples. As the level of evaporation increases, early eluting alkane components are lost and the relative abundance of the alkane pattern decreases. In highly evaporated samples (see Sect. 5.2.6), the PNA EIP is typically dominant and the alkane EIP in some gasolines may also be strong. Due to regional variation in alkane content, it is important for an examiner to collect gasoline samples from their region.

In neat and lightly evaporated samples (up to about 50%), there is a pattern of alkanes that elutes prior to C_8. Figure 5.3 consists of a selection of samples that show the variability of an early eluting (pre-C_8) chromatographic pattern. Based on this data, the early eluting pattern between C_6 and C_8 appears to be the result of a blend of at least two refinery streams, depicted as the "+" and "o" marked peaks in Fig. 5.3. The "o" peaks are known as alkylate refinery stream components. The patterns in chromatograms A through E suggest that there is a continuum of abundances for the alkylate stream group (strongest in chromatogram A) relative to the group marked with a "+" (strongest in chromatogram E). The relative abundance of the alkylate stream compounds appears somewhat independent of the abundance of the normal alkanes (marked on the vertical lines), although the normal alkanes may be a part of the "+" group. Further discussion on the early eluting alkane pattern is provided in Sect. 5.2.5.

In more weathered samples, the alkane content above C_8 can aid in the identification of gasoline. The variability in the alkane pattern above C_8 is mainly based on the relative differences in abundance of the normal alkanes and branched alkanes within the pattern, as seen in the alkane EIPs in Fig. 5.4. In the top chromatogram of Fig. 5.4 (#16), the normal alkanes dominate, while the branched alkanes are present at much lower abundance, similar to a distillate pattern. The alkane profiles lower in Fig. 5.4 show a decrease in normal alkane content relative to the branched content. In the bottom chromatogram of Fig. 5.4 (#21), the normal alkanes are greatly reduced, while the branched alkanes dominate. It is important to note that unless the distillate or isoparaffinic pattern stands out in the TIC above the broad aromatic pattern, it should be considered as part of the global gasoline pattern.

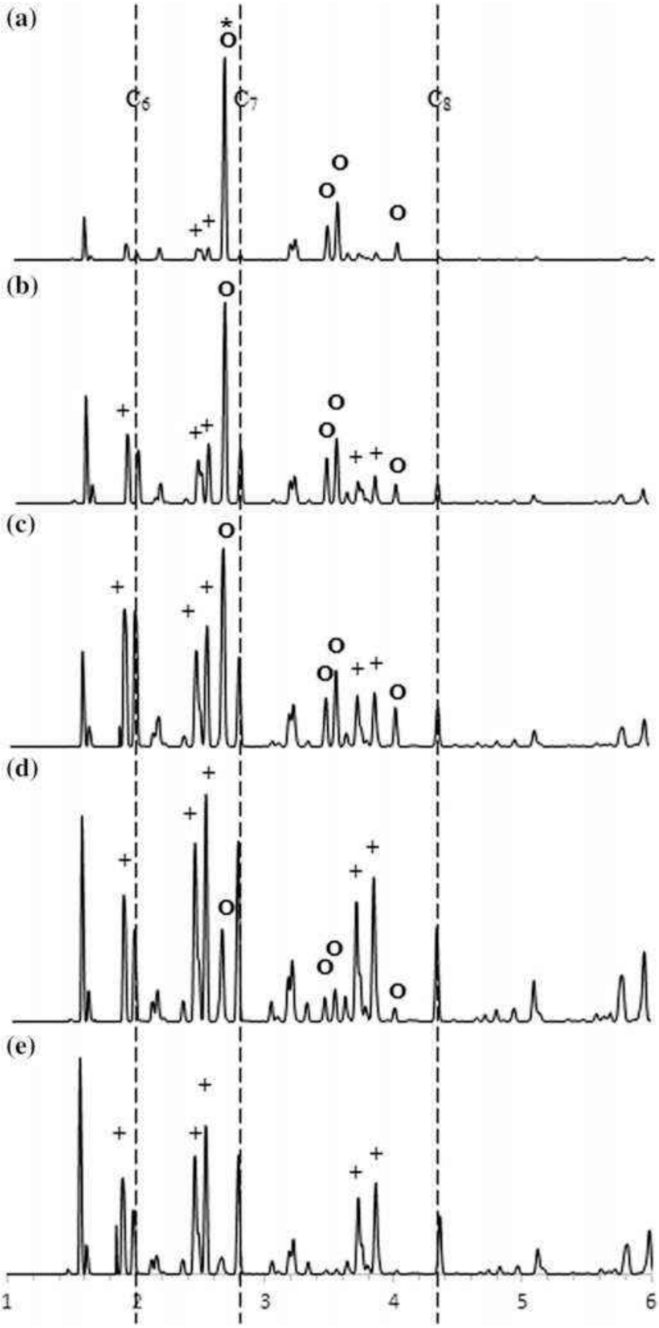


Fig. 5.3 Variability in the early alkane pattern, as observed in neat (unevaporated) gasolines. All marked peaks are branched alkanes; "O" indicates a known alkylate refinery stream component. Peak in chromatogram A marked with "*", just before heptane, is 2,2,4-trimethylpentane (isooctane). Chromatogram **a** is a 93-octane gasoline from Florida; **b** is a 93-octane gasoline from Ohio; **c** is an 87-octane gasoline from Delaware; **d** is an 87-octane gasoline from Ohio; and **e** is an 87-octane gasoline from Ohio

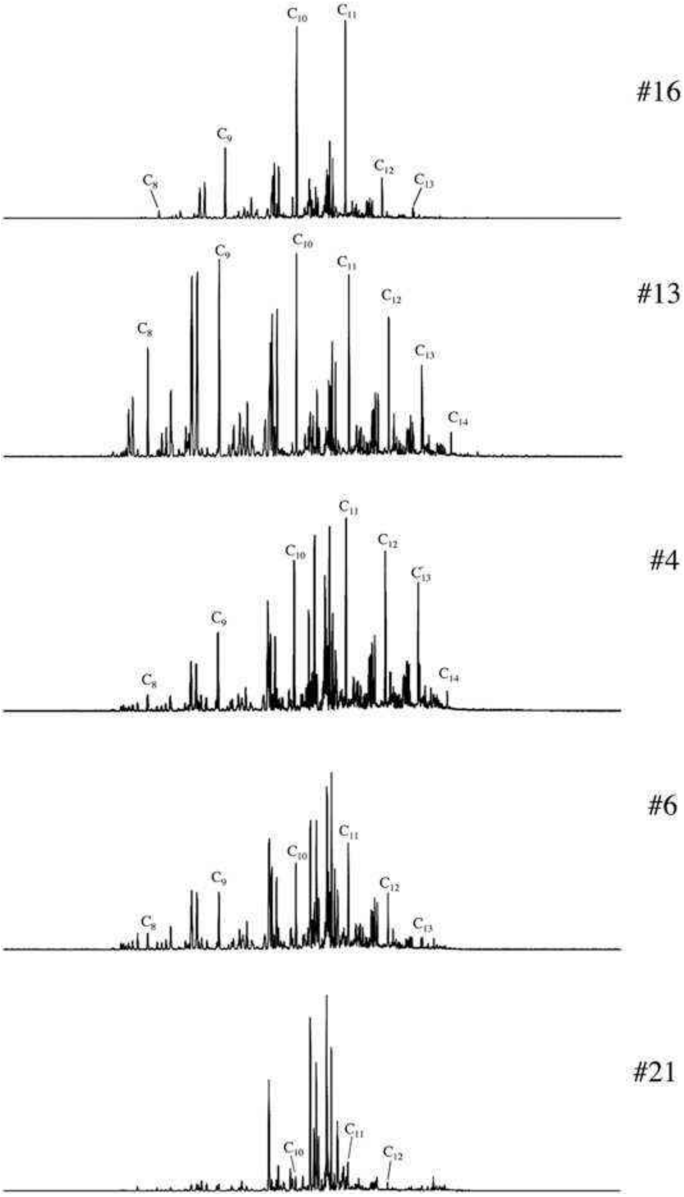


Fig. 5.4 Variability in the alkane EIP in 90% evaporated gasolines [5, Fig. 2]. Chromatogram #16 is an 87-octane gasoline from Ohio; #13 is an 87-octane gasoline from Ohio; #4 is an 89-octane gasoline from Florida; #6 is an 87-octane gasoline from Florida; and #21 is a 93-octane gasoline from Florida

5.2.4 Indane EIP Variability

The abundance of the indane EIP pattern in all but highly evaporated gasolines is relatively low compared to the aromatic and alkane abundances. As the level of evaporation increases, the prominence of the indane pattern increases.

While ASTM E1618-14 does not require that the indane pattern be reviewed, this pattern is characteristic of petroleum products and is quite consistent in its presentation when present. Figure 5.5 represents a typical indane pattern for neat (unevaporated) gasoline and some of the minor variability that is observed in these patterns. Chromatogram 5.5 (a) is a typical indane EIP for neat gasoline. Chromatogram 5.5 (b) is a neat sample where the response for C_1-alkylindanes is greater than indane, and C_2-alkylindanes are present (which is unusual for neat gasoline). Chromatogram 5.5 (c) is a sample with low levels of C_1-alkylindanes. Since the indane pattern does not fall in the light range of gasoline, it does not vary much for gasoline based on the level of evaporation, except when the gasoline is evaporated over 95%.

5.2.5 Other Patterns of Interest

The blending of various refinery streams, such as the isomerate, alkylate, naphtha, catalytically cracked naphtha, and pyrolysis gasoline (pygas) after hydrotreatment, can be the source of the alkane pattern discussed in Sect. 5.2.3. It has been suggested by Hendrikse et al. that the presence of alkylate and pygas refinery streams can be identified and used as supporting evidence in the identification of a refinery-based product (such as gasoline or aviation gas) [7, 8].

The alkylate refinery stream consists largely of branched alkanes. The extracted ion chromatograms (EICs) for the individual ions of *m/z* 57 and 71 can be utilized to identify the alkylate refinery stream [7, 8]. As previously discussed, chromatogram **a** in Fig. 5.3 represents a gasoline with the presence of an alkylate fraction (peaks identified with an "o"), while chromatogram **e** represents a gasoline with no alkylate fraction present. Figure 5.6 shows the EICs for *m/z* 57 and 71 for these same two gasolines. The presence of the alkylate refinery stream was detected in at least 99% of the gasoline samples within the Netherland's reference collection utilized in their study [8]. Within the 71 US gasolines that were investigated [6], approximately 70% showed the presence of an alkylate fraction.

Pygas is a by-product of ethylene production and can be added to gasoline as an octane enhancer [7]. Pygas is another refinery stream that can be identified in samples by reviewing the EIC for *m/z* 66. Pyrolysis gasoline is hydrotreated before blending with gasoline, resulting in the production of, among others, tetrahydrodicyclopentadiene (4H-DCPD), possibly in combination with dihydrodicyclopentadiene (2H-DCPD) and the remaining presence of unreacted dicyclopentadiene (DCPD) if the hydrotreatment was incomplete [7]. The presence of DCPD,

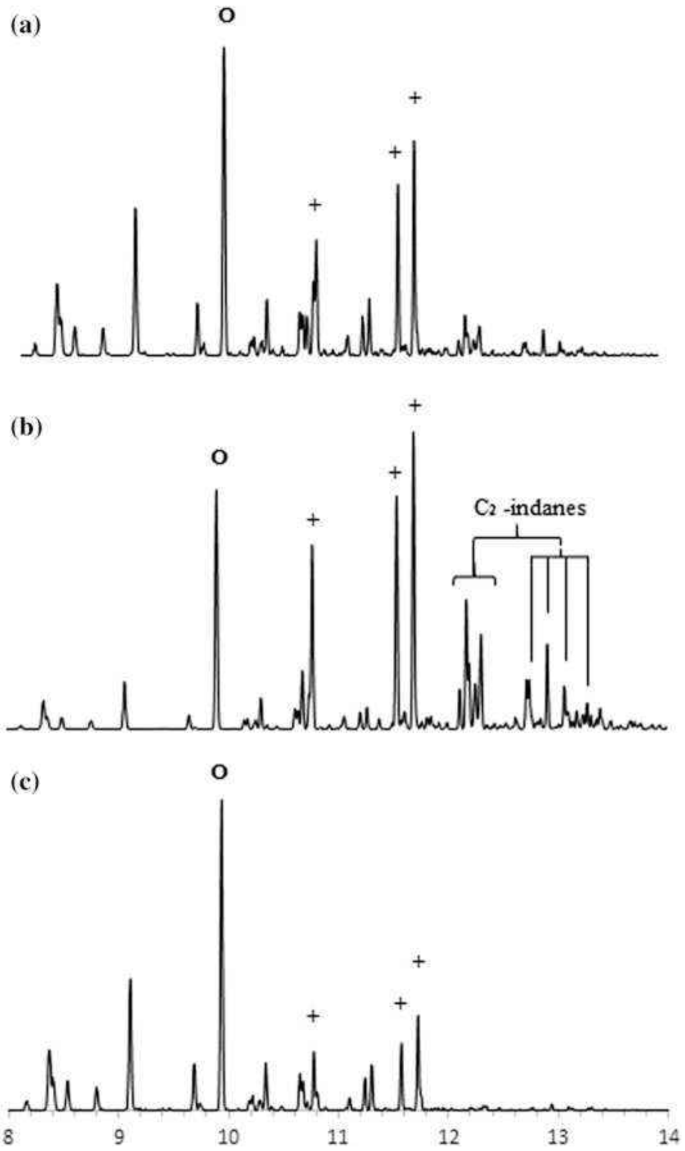


Fig. 5.5 Variability of indane response in neat gasoline. "O" marks indane, and "+" marks the C_1-alkylindanes. Chromatogram **a** is of an 87-octane gasoline from Ohio; **b** is of an 87-octane gasoline from Texas; and **c** is of an 85-octane gasoline from Colorado

2H-DCPD, and/or 4H-DCPD was indicated in approximately 25% of the US gasolines studied [6]. In 18% of the sampled US gasolines, the presence of a DCPD component was readily evident in the *m/z* 66 EIC (such as in Fig. 5.7a, b). In general, the majority of the gasolines from the US survey with indications of pygas

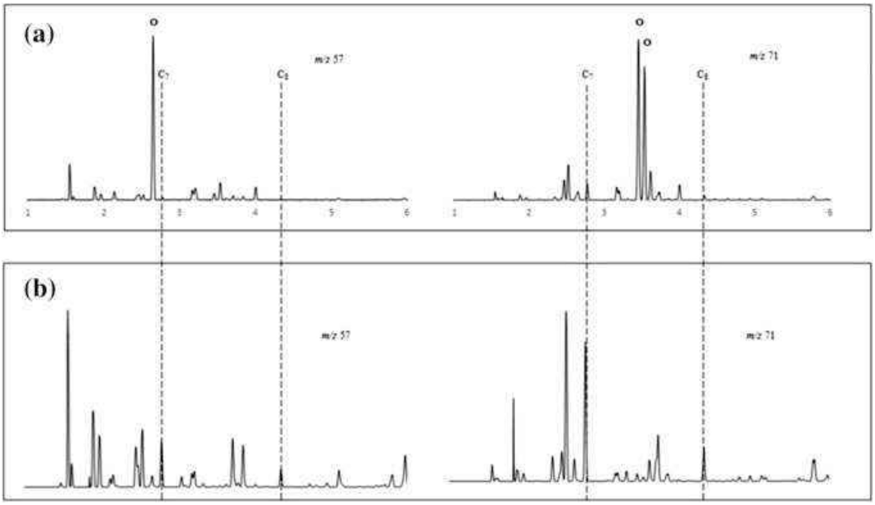


Fig. 5.6 Extracted ion chromatograms for *m/z* 57 and 71, for a gasoline that contains alkylate (**a**), the same gasoline as is shown in Fig. 5.3 (**a**); and a gasoline that does not contain alkylate (**b**), the same gasoline as is shown in Fig. 5.3 (**b**); "o" indicates a known alkylate refinery stream component

were lower (e.g., 87 or 89) octane samples [6]. It has been suggested that the presence of components consistent with pygas can be used to support the identification of a refinery product [7].

5.2.6 Variability in Highly Evaporated Gasolines

As gasoline is evaporated, the aromatic profile typically remains the dominant profile, until about 95% evaporation. Usually, once the C_3-alkylbenzenes have evaporated, the later eluting PNA and/or alkane contributions are most abundant. Variability in heavily evaporated gasolines generally stems from the ratio of these two EIPs.

In a review of the data from 71 highly evaporated (98% evaporated or higher) US gasolines, some general trends were observed. The ratio of PNAs to alkanes in highly evaporated gasoline is much greater than the ratio observed in heavy petroleum distillates (neat or evaporated). In highly evaporated gasoline, the PNA: alkane EIP ratio is in the range of 5:1–1:5, while in heavy petroleum distillates (neat or evaporated), the ratio is in the range of 1:15–1:30 or more.

Five general groups were observed within the 71 samples examined:

1. TIC dominated by C_1-alkylnaphthalenes, with alkane content, possibly with n-C_{13} visible in the TIC (Fig. 5.8). The pattern in the alkane EIP is similar to a distillate. This response is similar to the average gasoline residue pattern reported by Sandercock [9].

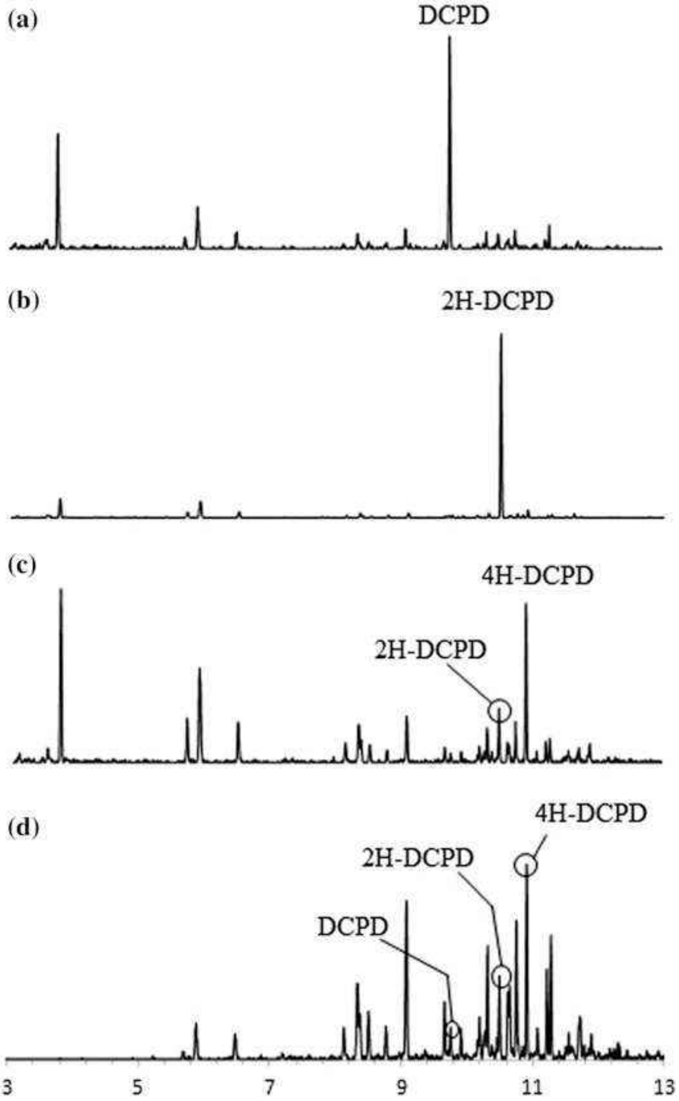


Fig. 5.7 Extracted ion chromatogram for *m/z* 66, indicating the presence of the pygas refinery product with DCPD, 2H-DCPD, and 4H-DCPD in neat, unevaporated gasolines (**a**—87-octane from Florida, **b**—87-octane from Texas, and **c**—87-octane from Texas) and the presence of all three in a 90% evaporated gasoline (**d**—87-octane from South Carolina)

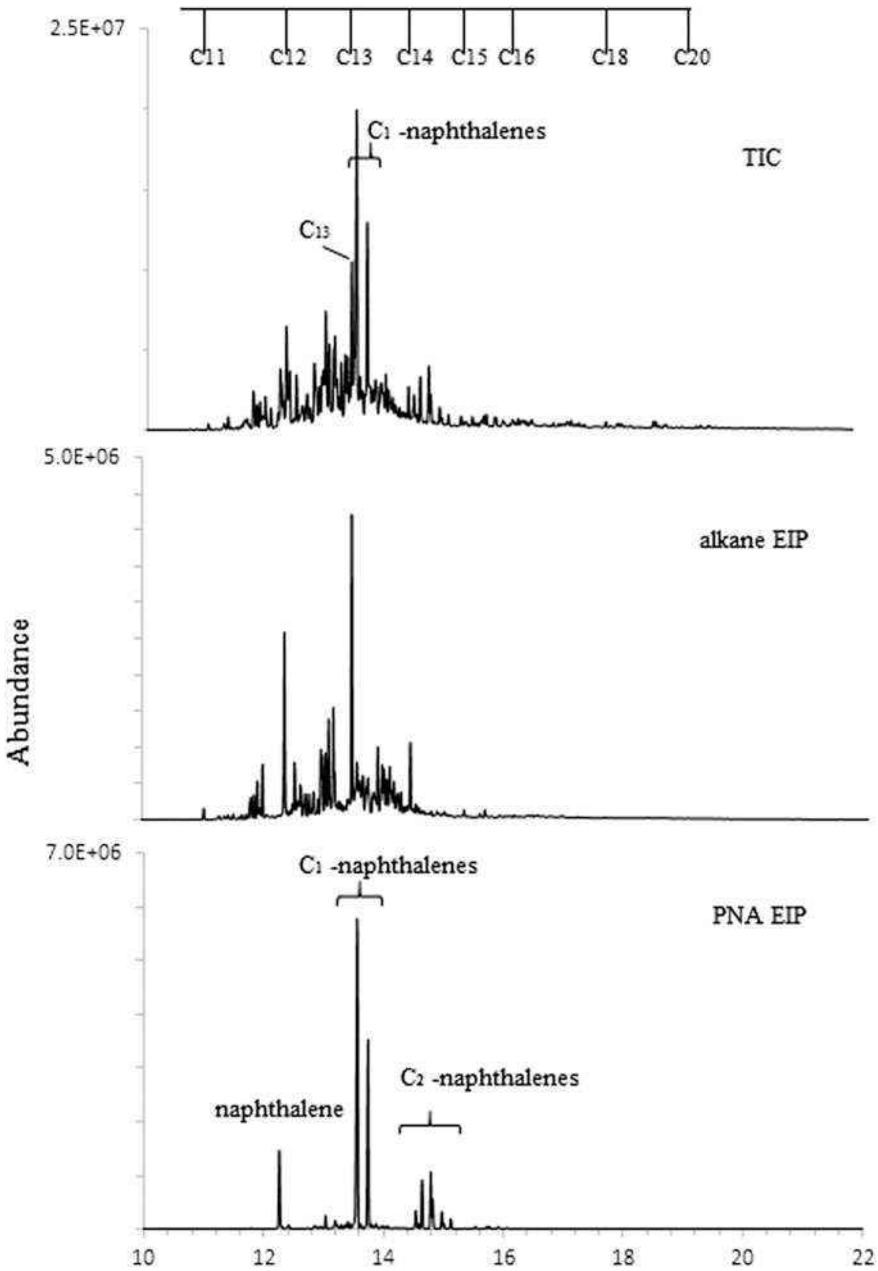


Fig. 5.8 Example of a highly evaporated gasoline dominated by C_1-alkylnaphthalenes, in an 89-octane gasoline from Florida, evaporated over 99%

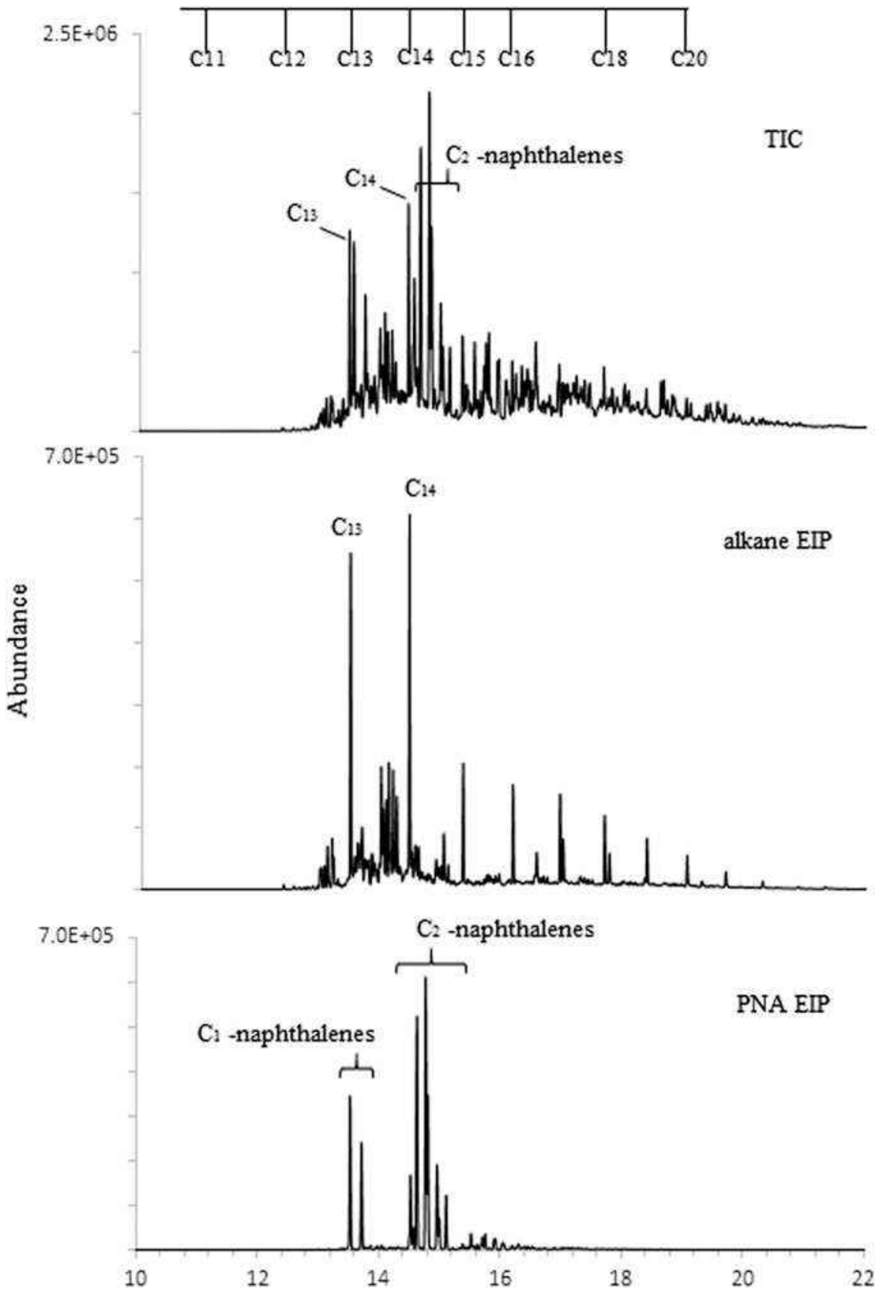


Fig. 5.9 Example of a highly evaporated gasoline dominated by C_1- and C_2-alkylnaphthalenes, in an 87-octane gasoline from Ohio, evaporated over 99%

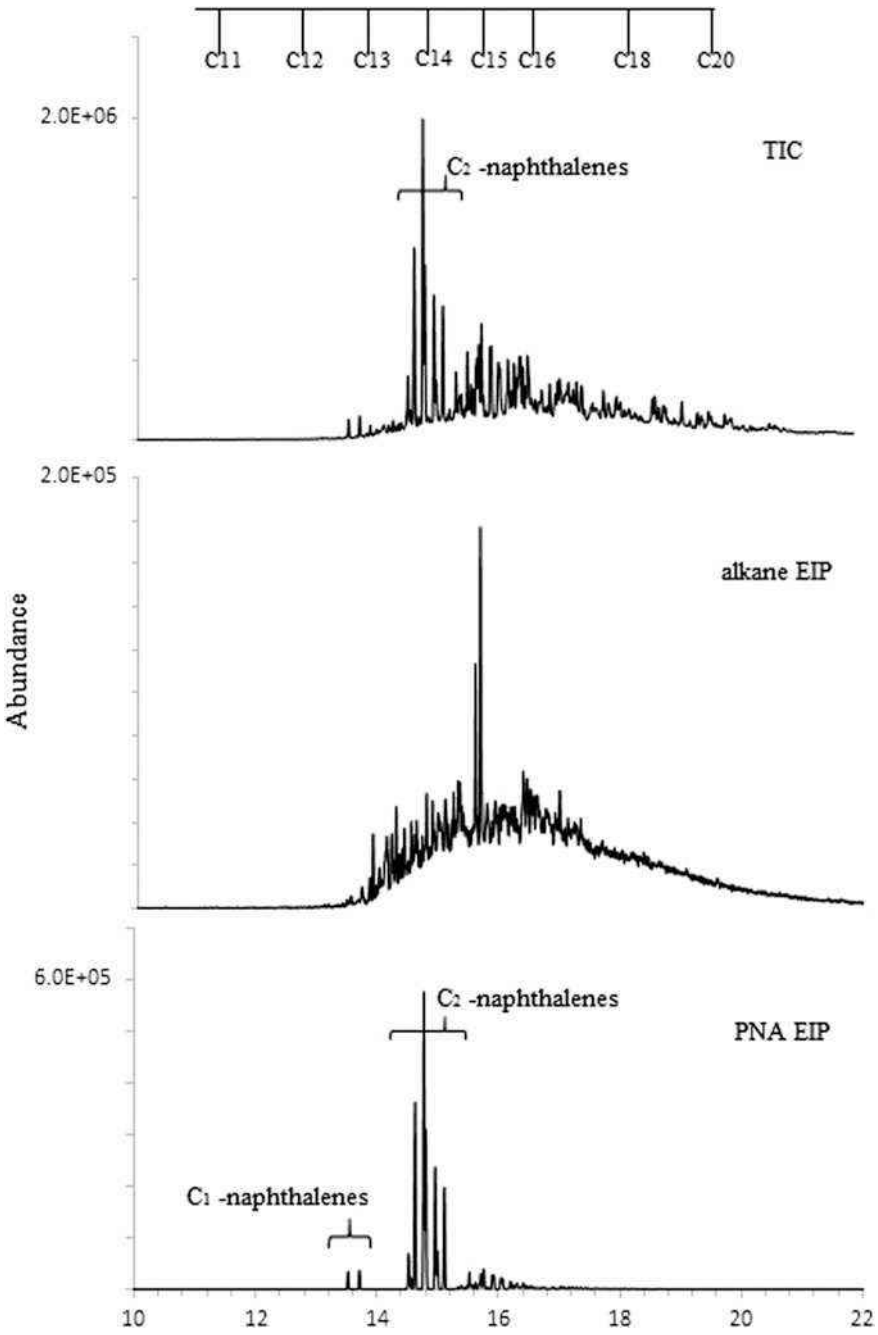


Fig. 5.10 Example of a highly evaporated gasoline dominated by C_2-alkylnaphthalenes, with unresolved alkanes, in an 87-octane gasoline from Delaware, evaporated over 99%

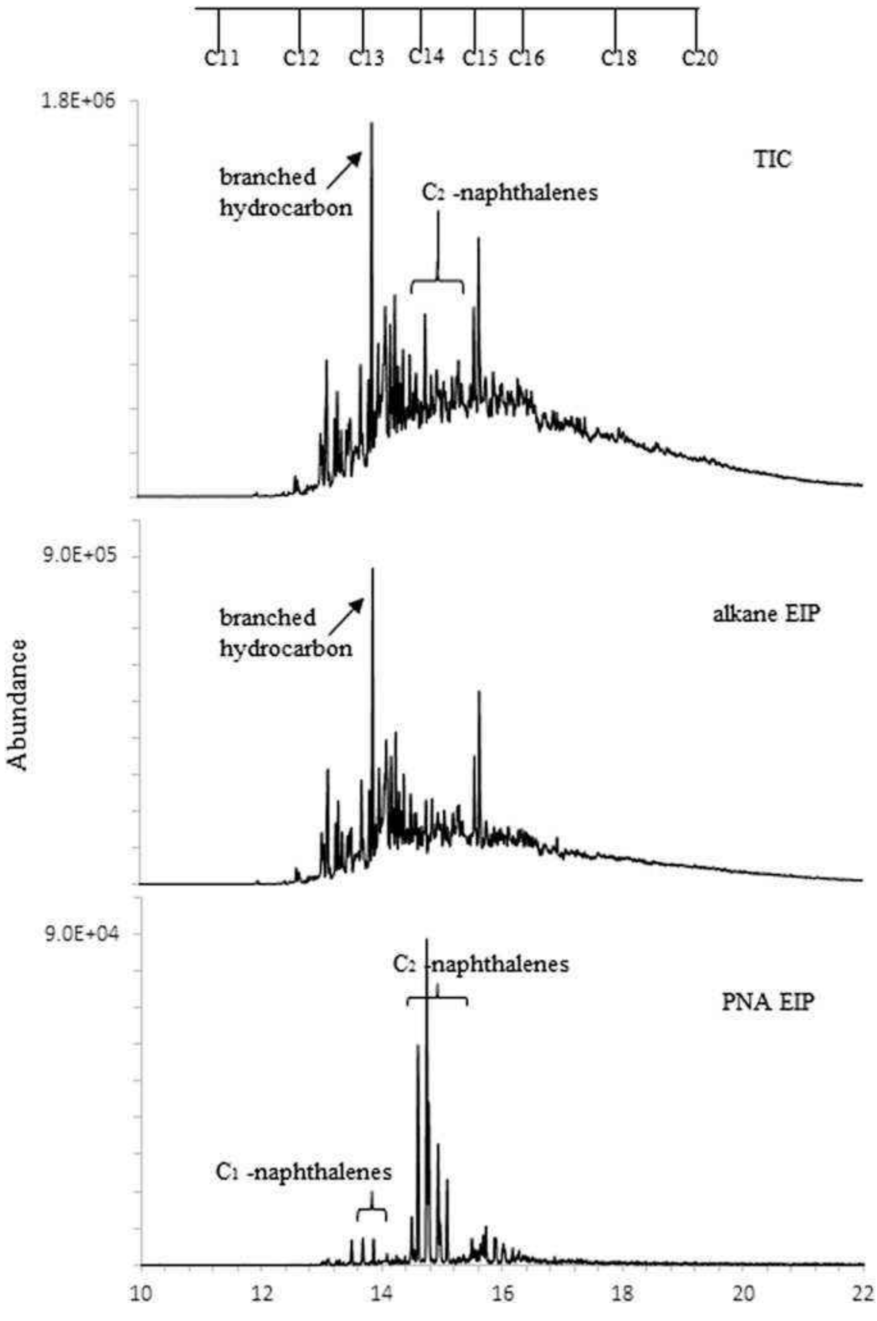


Fig. 5.11 **Example of a highly evaporated gasoline** dominated by an unresolved envelope, in a 91-octane gasoline from California, evaporated over 99%

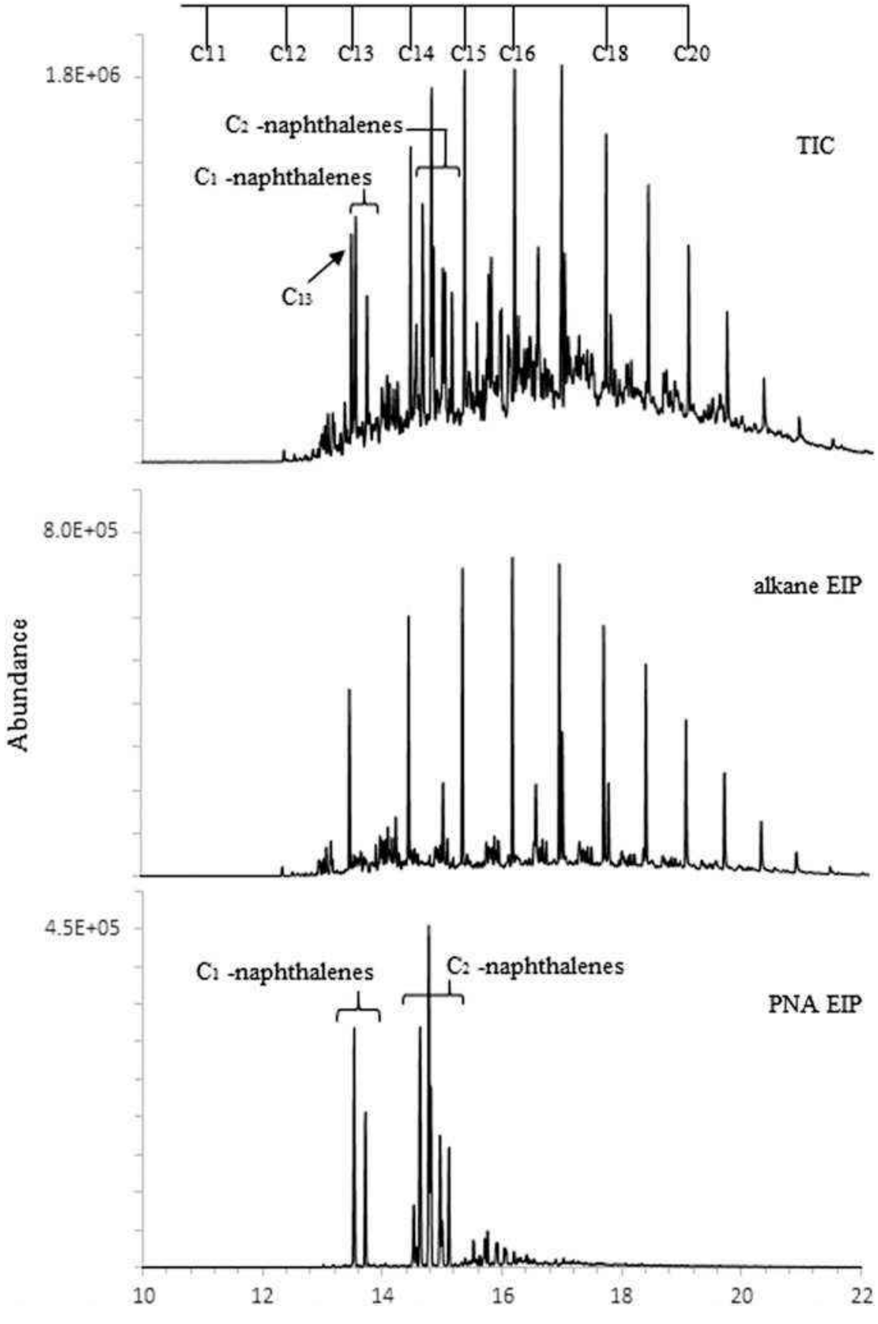


Fig. 5.12 Example of a highly evaporated gasoline dominated by a paraffinic response with substituted naphthalenes also present, in an 87-octane gasoline from South Carolina, evaporated over 99%

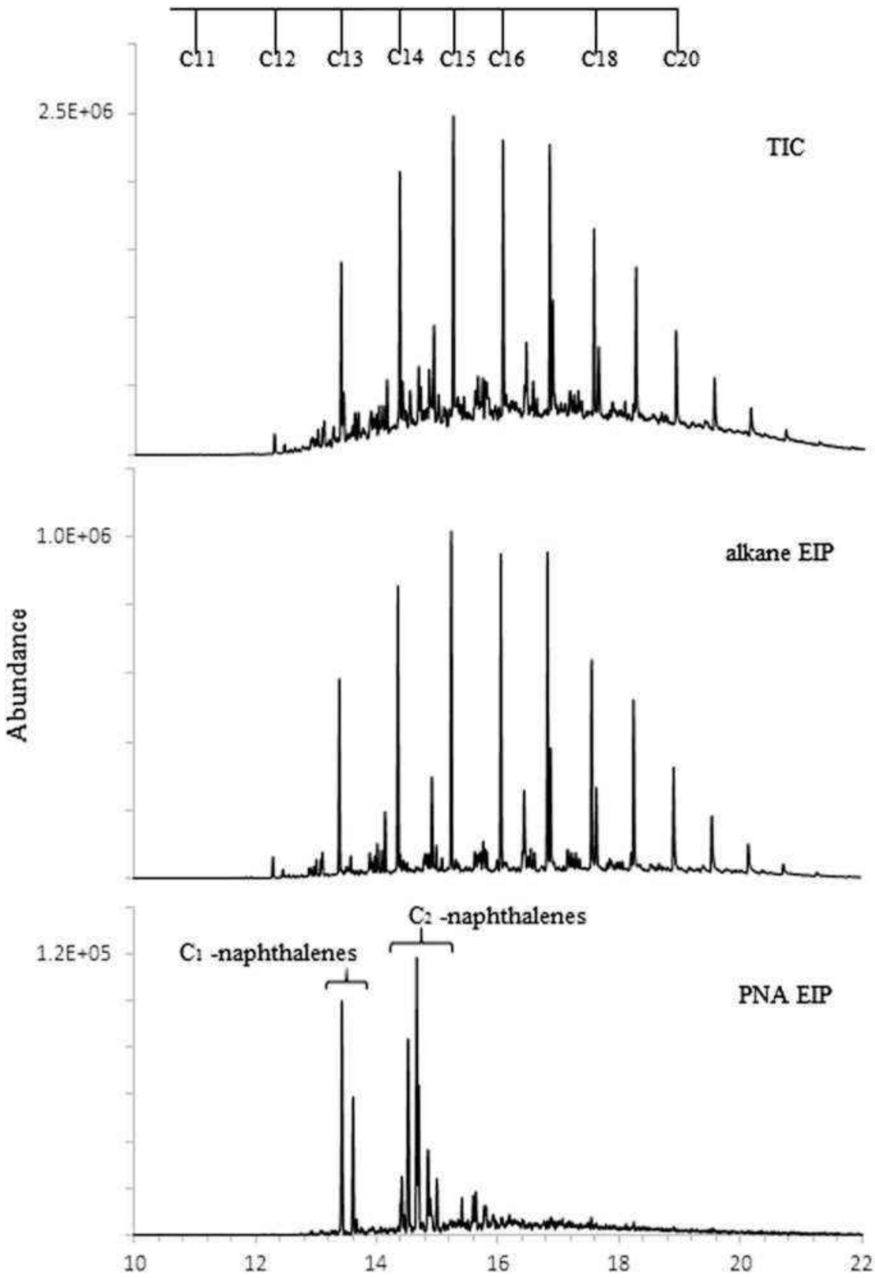


Fig. 5.13 Example of a highly evaporated gasoline that would be difficult to differentiate from a heavy petroleum distillate, in an 85-octane gasoline from Colorado, evaporated over 98%

2. TIC dominated by C_1- and C_2-alkylnaphthalenes, with alkane content that may be visible in the TIC (Fig. 5.9). The pattern in the alkane EIP is somewhat similar to a distillate.
3. TIC dominated by C_2-alkylnaphthalenes, with an unresolved envelope of alkane content (Fig. 5.10).
4. TIC that is mostly described as an unresolved envelope, with (usually) dominant alkane content in the alkane EIP that mirrors the TIC (Fig. 5.11).
5. TIC dominated by alkane content with characteristics similar to a distillate and substituted naphthalenes also present, which may or may not be readily evident in the TIC (Fig. 5.12).

It is important to note that these five patterns are general trends, but are not all encompassing of all evaporated gasolines. For example, one of the highly evaporated gasolines in the US study [6] could be correctly identified as a heavy petroleum distillate (Fig. 5.13). The PNA: alkane EIP ratio was 1:10, and the pattern eluted late enough that there was no useful information in the aromatic or indane ratios.

5.2.7 Additional Gasoline Resources

Additional examples of gasoline can be found in various references [6–13]. Three of these are gasoline surveys, summarizing the data of relatively large samplings of gasolines with various points of focus [6, 9, 13]. These surveys also include samples that exhibited unusual characteristics for which the discussions and level of detail were beyond the scope of this text.

Additionally, the International Database of Ignitable Liquids [14] contains 15 gasolines, most of which were considered to be atypical representations of gasoline from their respective points of origin. For those outside of North America, the International Database also provides a resource of examples of products that contain ignitable liquids that are available in other parts of the world.

5.3 Use of the Descriptors Light, Medium, and Heavy

ASTM E1618-14 describes the division of all nongasoline classes into light, medium, and heavy subclasses based on carbon range [5]. The carbon ranges for light, medium, and heavy are C_4–C_9, C_8–C_{13}, and C_9–C_{20+}, respectively. Some examiners only use the light, medium, and heavy descriptors in relation to petroleum distillates, while others utilize the descriptors for all classes except gasoline. In order to include more information about the identification of an ignitable liquid in case notes, discussions, and reports, the use of the subclass descriptors should be considered good practice and is utilized throughout the rest of this chapter.

5.4 Petroleum Distillates

Petroleum distillates are generally recognizable by their Gaussian distribution of normal alkanes in the TIC (see Chap. 2). Petroleum distillates contain normal alkanes, branched alkanes, cyclic alkanes, aromatic compounds, and polynuclear aromatic compounds. The presence and abundance of these compounds vary between the subclass of light, medium, and heavy. Within each subclass, there is variation in features such as the carbon range, extent of symmetry in the distribution of normal alkanes, relative concentration of branched alkanes to normal alkanes, and the relative concentration of aromatic content to alkane content. The relative abundance between compound classes is not always apparent in the TIC. Comparison of relevant extracted ion profile (EIP) abundances provides a means of determining the relative ratios.

5.4.1 Light Petroleum Distillates (LPDs)

LPDs may not always exhibit the recognizable Gaussian normal alkane pattern nor contain many aromatic compounds compared to MPDs and HPDs [5]. This is due to the small carbon range of low molecular weight compounds. Figure 5.14 shows two LPDs that predominantly contain branched, cyclic, and normal alkanes. However, the branched alkanes in LPD (a) are more abundant than LPD (b) as demonstrated in the alkane EIP. LPD (a) contains toluene, ethylbenzene, m-xylene, and o-xylene, whereas LPD (b) does not contain any aromatic compounds and is considered to be “de-aromatized.” In addition, LPD (a) shows a relatively narrow range, whereas LPD (b) spans a wider carbon range.

5.4.2 Medium Petroleum Distillates (MPDs)

Medium petroleum distillates typically have a symmetrical Gaussian pattern of normal alkanes. The relative abundances of aromatic compounds to alkanes are a major type of variation between MPDs. Aromatic compounds that elute in the medium carbon range include C_2-, C_3-, and C_4-alkylbenzenes and the PNA naphthalene. Another type of variation is the relative abundances of branched alkanes to the normal alkanes. In addition, there is variation in the breadth of the carbon ranges and in the symmetry of the chromatographic patterns. Figure 5.15 demonstrates the variation between three MPDs. MPD (a) is an example of a classic MPD with a Gaussian pattern consisting of three to four normal alkanes with a lower abundance of branched alkanes. MPD (b) has a narrow carbon range, a lower abundance of aromatic compounds, and a branched alkane as a major peak. MPD (c) has a wide carbon range and an asymmetric chromatographic profile.

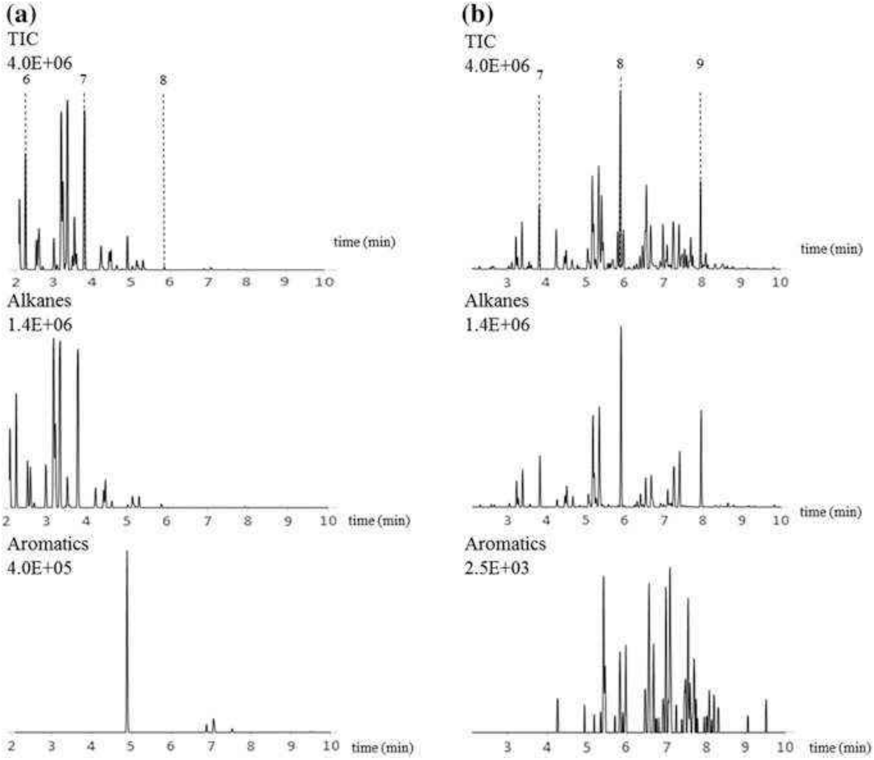


Fig. 5.14 Comparison of two light petroleum distillates. Both contain similar abundances of normal alkanes; however, their branched alkane and aromatic content are not the same. LPD **a** contains toluene, ethylbenzene, m/p-xylene, and o-xylene, whereas LPD **b** does not contain any aromatic compounds

Figure 5.16 compares a classic petroleum distillate (a) to a dearomatized petroleum distillate (b). Visual comparison of the TICs indicates some differences between the two MPDs; however, the EIPs provide a clearer indication of the differences. MPD (a) contains C_3- and C_4-alkylbenzenes at a typical abundance for distillates. MPD (b) contains the same aromatic compounds, but the abundances are an order of magnitude lower than in the classic distillate. Evaluation of the alkane EIPs indicates that the relative concentration of branched alkanes to normal alkanes is greater in (a) compared to (b). Despite differences in aromatic content, branched alkane content, and carbon range, all of the ignitable liquids in Figs. 5.15 and 5.16 are considered MPDs.

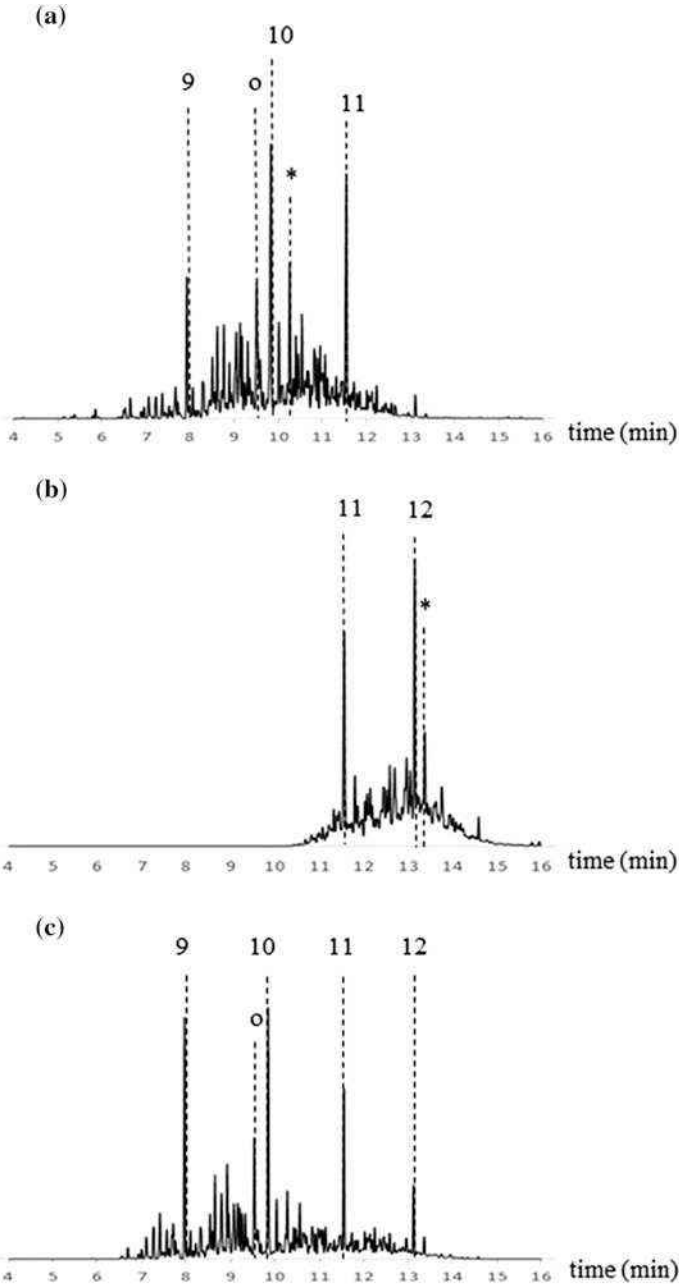


Fig. 5.15 Total ion chromatograms of medium petroleum distillates with variations in carbon range, symmetry of chromatographic profiles, and relative chemical composition. MPD (**a**) has a classical chemical composition and chromatographic pattern. MPD (**b**) has a narrow carbon range, an indication of a lower abundance of aromatic compounds and a branched alkane as a major peak. MPD (**c**) has a wide carbon range and an asymmetric chromatographic profile. Numbers represent normal alkanes, * represent branched alkanes, and o represent aromatic compounds

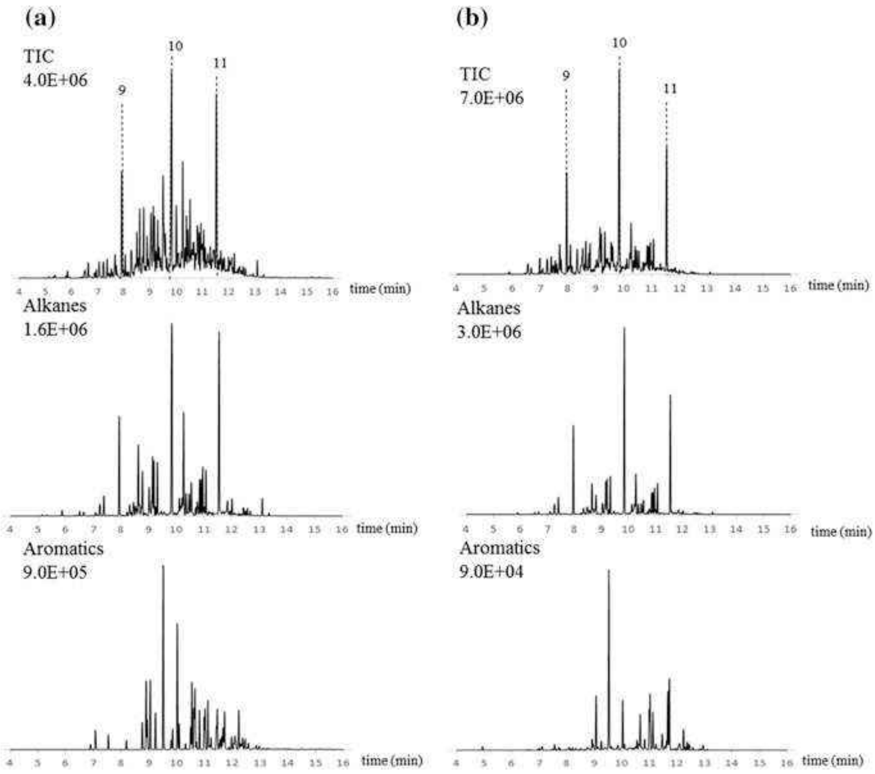


Fig. 5.16 Comparison of two medium petroleum distillates. Both contain similar abundances of normal alkanes; however, their branched alkane and aromatic content is not the same. The relative concentration of branched alkanes to normal alkanes is greater in (**a**) compared to (**b**). MPD (**a**) contains C3- and C4-alkylbenzenes at a typical abundance for distillates. MPD (**b**) contains the same aromatic compounds, but the abundances are low for a typical distillate

5.4.3 Heavy Petroleum Distillates (HPDs)

As with MPDs, heavy petroleum distillates typically have a Gaussian distribution of normal alkanes in the TIC. Much of the variation within the HPD class is associated with the diverse spread in the carbon ranges. The Ignitable Liquids Reference Collection (ILRC) database contains 69 HPDs [11]. The broadest carbon range contains nineteen normal alkanes (n-octane to n-hexacosane), and the narrowest contains four normal alkanes (n-undecane to n-tetradecane). The most common carbon range in the ILRC is n-octane to n-heptadecane. Other types of variation are the symmetry of the TIC pattern, relative concentration of branched alkanes to normal alkanes, and the relative concentration of aromatic compounds to alkanes. Examples of these variations are shown in Fig. 5.17. HPD (a) has a broad carbon range with a symmetric chromatographic pattern. HPD (b) has a narrow carbon

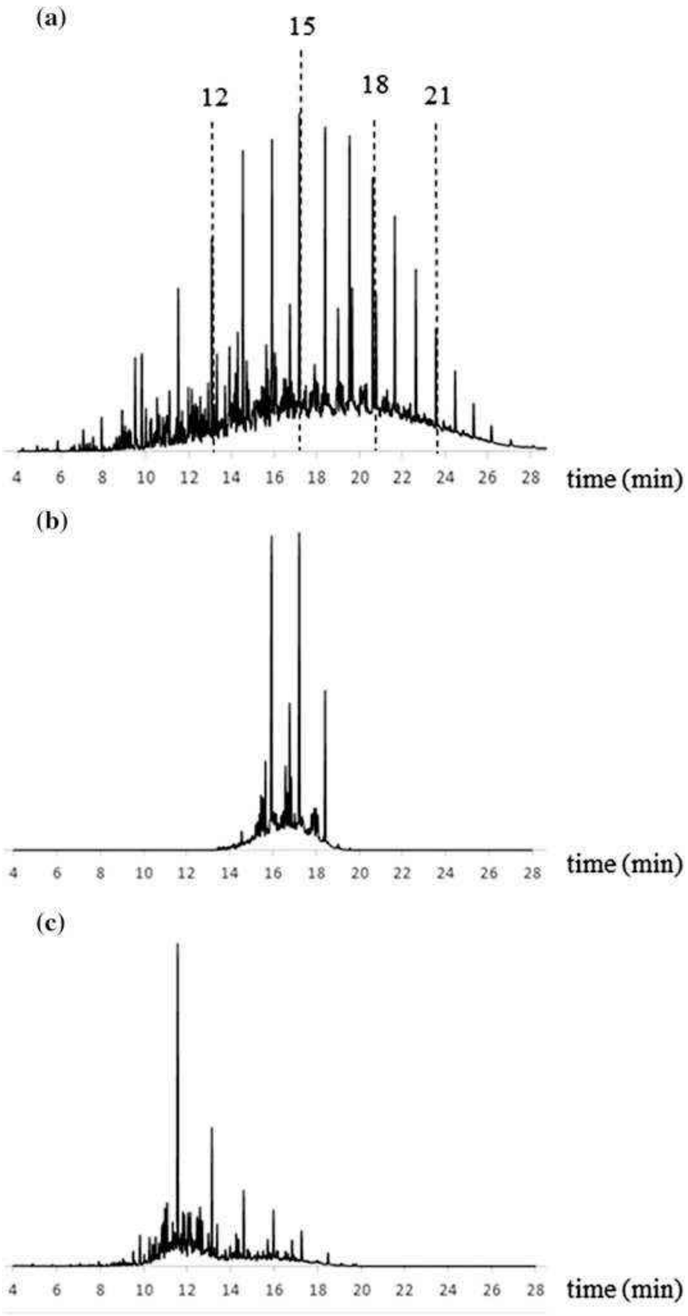


Fig. 5.17 Total ion chromatograms of heavy petroleum distillates with variations in carbon range, symmetry of chromatographic profiles, and relative chemical composition

range with a symmetric chromatographic pattern. HPD (c) has a typical carbon range with an asymmetric chromatographic pattern.

Depending on the carbon range, HPDs contain the same aromatic compounds as the MPDs and may contain C_1- and C_2-alkyl-substituted naphthalenes PNA. Again, the relative abundance of aromatic content to alkane content is a type of variation within the subclass. Figure 5.18 demonstrates the variability in carbon range and aromatic content of HPDs. HPD (a) has a carbon range from n-octane to n-hexacosane and contains a relative abundance of C_3- and C_4-alkylbenzenes (aromatic compounds) to alkanes typical of distillates. HPD (b) has a carbon range from n-decane to n-hexadecane, and even though there is a pattern in the aromatic EIP, there were no aromatic compounds identified. HPD (c) has a carbon range from n-nonane to n-hexadecane with the C_3-alkylbenzenes visible in the TIC. HPD (c) has a higher abundance of aromatic compounds to alkanes than a and b.

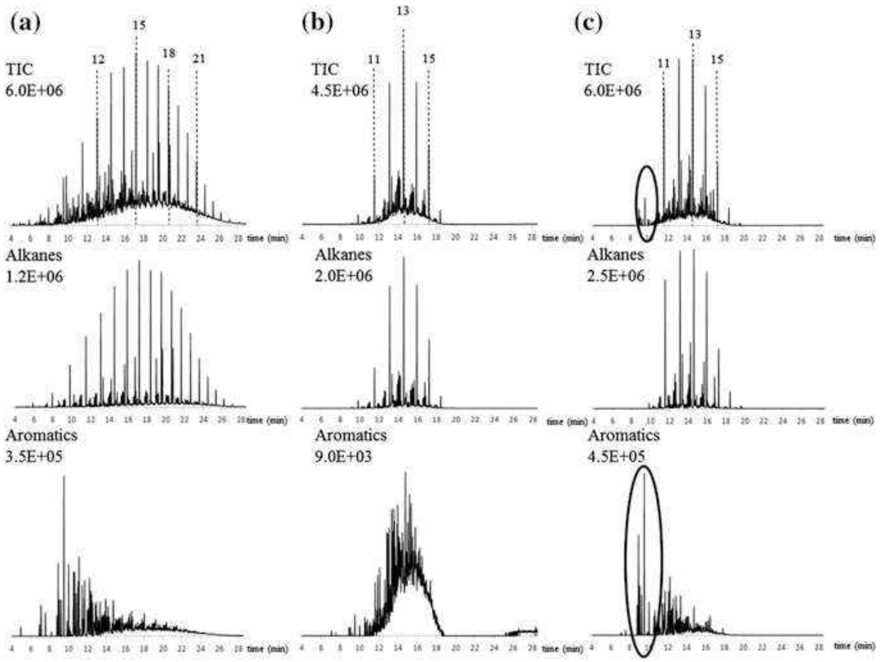


Fig. 5.18 Comparison of three heavy petroleum distillates. HPD (**a**) has a typical relative abundance of alkanes to aromatics for distillates. HPD (**b**) contains no aromatic compounds even though there is a pattern. HPD (**c**) has a higher abundance of aromatic compounds (within the circled area) than alkanes

5.5 Naphthenic–Paraffinic Products

Naphthenic–paraffinic (NP) **products** predominantly contain branched and cyclic alkanes, as discussed in Chap. 2. While NP products may contain normal alkanes, they are usually in lower abundance compared to the other alkanes. If aromatic compounds are present, they will be a minor constituent. Naphthenic–paraffinic products are mainly in the medium and heavy carbon ranges. Slight variations observed in NP products are mostly due to the breadth of the carbon range and the relative abundance of normal alkanes compared to branched and cyclic alkanes. Total ion chromatograms of two heavy and one medium naphthenic–paraffinic products in Fig. 5.19 demonstrate some of the variability within the class. NP (a) and NP (b) have the same carbon range of n-nonane to n-pentadecane (heavy); however, (a) does not contain any normal alkanes whereas (b) contains three normal alkanes. The n-undecane in NP (c) is the second most abundant compound; however, other major peaks are either branched or cyclic alkanes. The normal alkanes present in (b) and (c) are less abundant compared to a distillate with a similar carbon range.

As shown in Fig. 5.19, the patterns of heavy NP products appear as unresolved envelopes. The alkane EIPs as shown in Fig. 5.20 are helpful in visualizing the alkane patterns and estimating the abundance of normal alkanes, if present.

5.6 Isoparaffinic Products

Isoparaffinic products are composed solely of branched alkanes (see Chap. 2). Figure 5.21 contains TICs of a light (a), medium (b), and heavy (c) isoparaffinic product demonstrating the variation within this class. The number of branched alkanes increases with molecular weight and is due to the increase in the number of possible isomers. As the number of branched alkanes increases, the ability to resolve them decreases, which results in the appearance of an unresolved chromatographic pattern.

5.7 Normal Alkane Products

Normal alkane products are composed exclusively of normal alkanes (see Chap. 2). Normal alkanes are mainly in the medium and heavy carbon ranges. Variation within this class is minimal given the simplicity of the chemical composition. The variation observed is mainly in the number of the normal alkanes present and their relative abundance to one another as shown in Fig. 5.22.

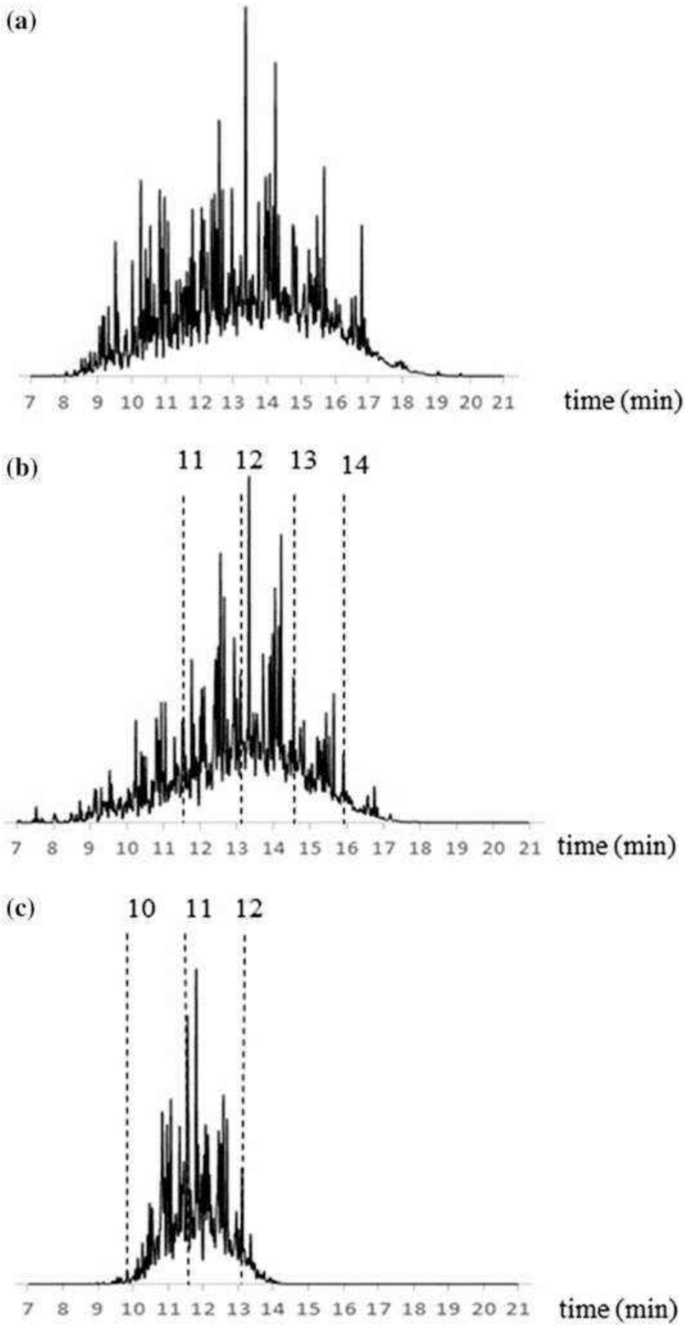


Fig. 5.19 TIC comparison of two heavy and one medium naphthenic–paraffinic products. NP (**a**) does not contain any normal alkanes, NP (**b**) contains four normal alkanes, and NP (**c**) contains three normal alkanes

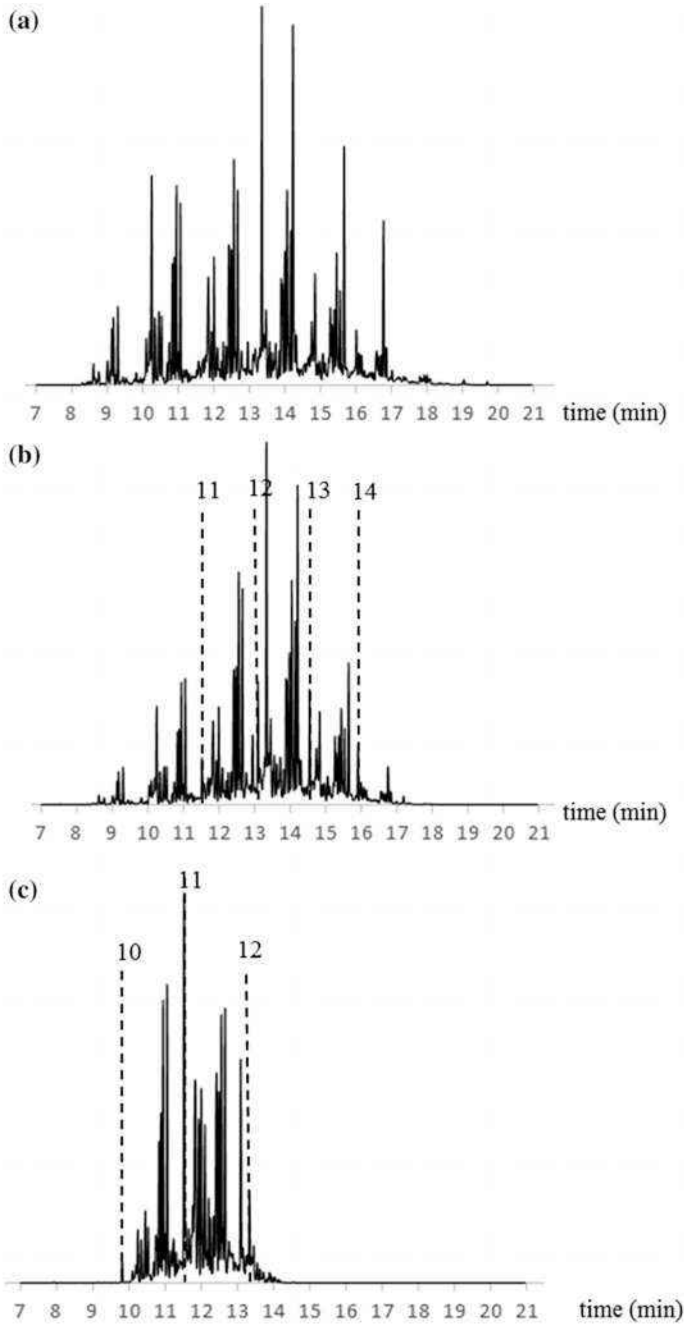


Fig. 5.20 Alkane EIPs of NP products in Fig. 5.19. NP (**a**) does not contain any normal alkanes, NP (**b**) contains four normal alkanes, and NP (**c**) contains three normal alkanes

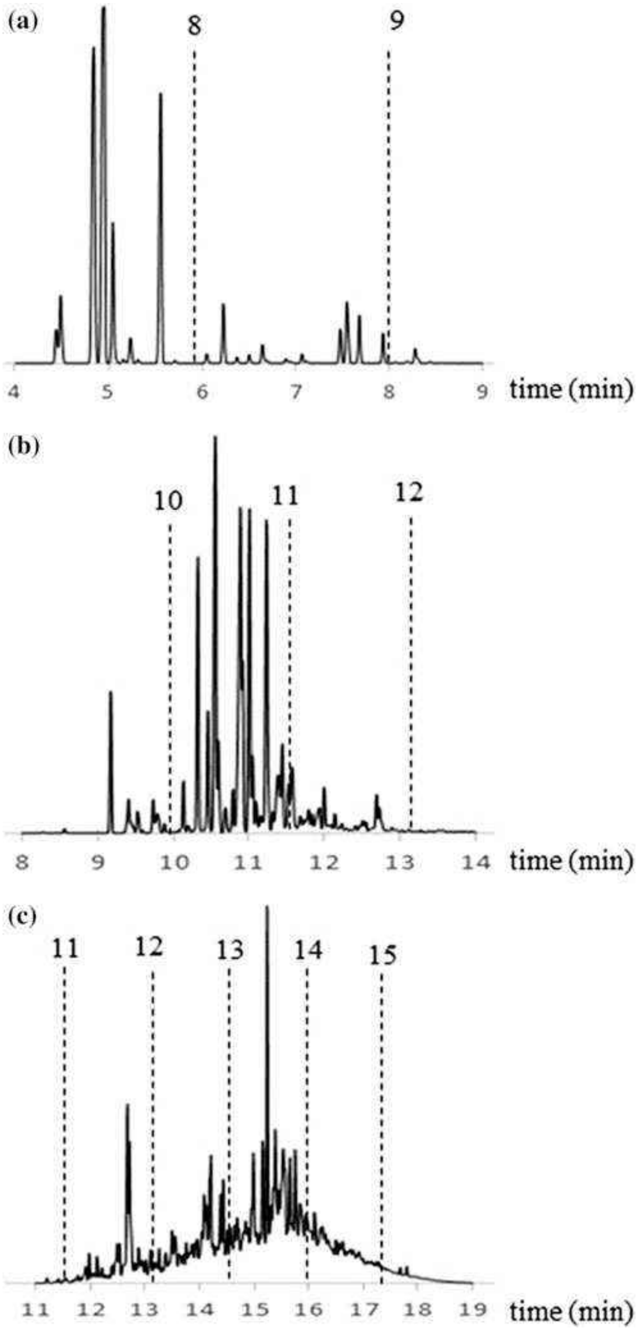


Fig. 5.21 Total ion chromatograms of a light (**a**), medium (**b**), and heavy (**c**) isoparaffinic product

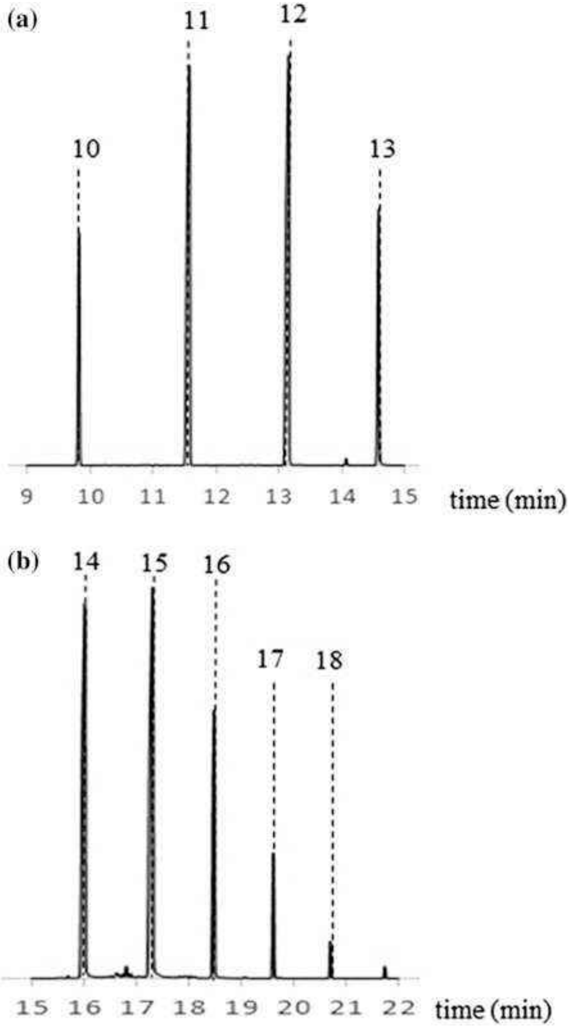


Fig. 5.22 Total ion chromatograms of two normal alkane products with different normal alkane compounds

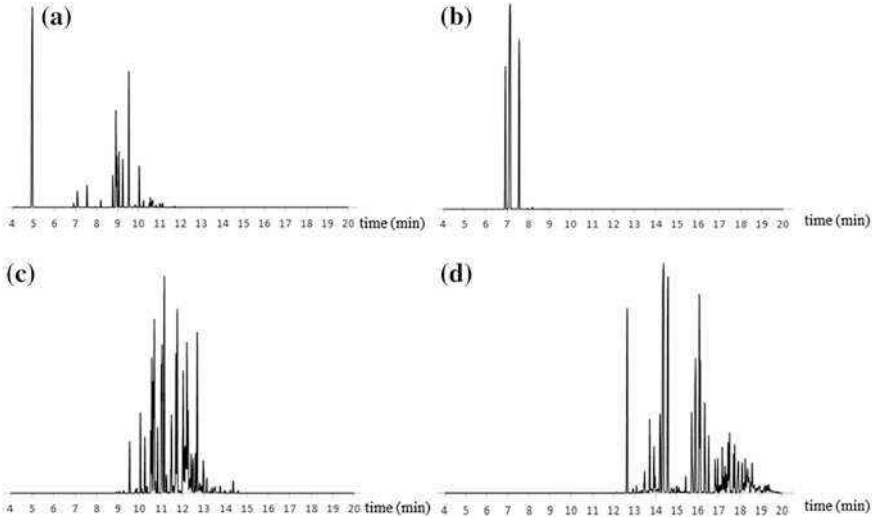


Fig. 5.23 Total ion chromatograms of a light–medium (**a**), light (**b**), medium (**c**), and heavy (**d**) aromatic product

5.8 Aromatic Products

Aromatic products contain exclusively aromatic and/or polynuclear aromatic compounds depending on the carbon range (see Chap. 2). Most light aromatic products contain toluene and/or C_2-alkylbenzenes. Medium aromatic products can contain combinations of C_2-alkylbenzenes, C_3-alkylbenzenes, C_4-alkylbenzenes, naphthalene, and methylnaphthalenes. Aromatic products with narrow carbon ranges typically contain a single group, such as the C_3-alkylbenzenes; those with larger carbon ranges contain several groups such as C_2-, C_3-, and C_4-alkylbenzenes. Heavy aromatic products are less common and contain exclusively polynuclear aromatic compounds. In Fig. 5.23, (a) is a light-to-medium aromatic product that contains toluene, C_2-, C_3-, and C_4-alkylbenzenes. Typically, the breadth of the aromatic pattern differentiates gasoline from aromatic products; however, in this particular case, the absence of alkanes differentiates this aromatic product from gasoline. Aromatic product (b) is a typical light aromatic product containing C_2-alkylbenzenes. The medium aromatic product (c) contains C_3-alkylbenzenes, C_4-alkylbenzenes, naphthalene, and C_1-alkylnaphthalenes. The most abundant compounds in the heavy aromatic product (d) are polynuclear aromatic compounds consisting of naphthalene, C_1-alkylnaphthalenes, and C_2-alkylnaphthalenes.

5.9 Oxygenated Solvents

Oxygenated solvents contain one or more oxygenated compounds of significant abundance and may include other compounds or products (see Chap. 2). Oxygenated compounds typically identified in ignitable liquids include alcohols, ketones, and esters [5]. Other oxygenated compounds such as aldehydes and phenols are identified in fire debris but originate from the matrix as discussed in Chap. 3.

Since the identification of a major constituent as an oxygenated compound is the main criteria to classify an ignitable liquid as an oxygenated solvent, there is the potential for a considerable amount of variation. Some oxygenated solvents contain exclusively oxygenated compounds, some contain a handful of compounds including an oxygenated compound, and some contain an oxygenated compound(s) with an ignitable liquid of another classification, as shown in Fig. 5.24. Oxygenated solvent (a) is solely composed of oxygenated compounds. Oxygenated solvent (b) contains several oxygenated compounds and a mixture of various other compounds. Oxygenated solvent (c) contains a medium aromatic product and a single oxygenated compound. Laboratory protocols will vary as to how to approach the interpretation and reporting of debris that appears to contain a mixture that includes an oxygenate(s).

5.10 Miscellaneous

For ignitable liquids that do not meet the criteria of a specific classification, there is a **miscellaneous** category. Ignitable liquids typically categorized as miscellaneous typically fall into three categories: (1) those that are not petroleum-based such as turpentine and plant-based oils; (2) those with characteristics of more than one class; and (3) those that are characteristics of a class, but contain a significant contribution from a single compound not characteristic of the class. Figure 5.25 demonstrates by comparison of TICs and chemical composition only a few examples of the variation found in the miscellaneous category. There is substantial variation of the ignitable liquids in the miscellaneous category. Ignitable liquids (a) and (c) are turpentine and orange oil, both examples of natural nonpetroleum-based ignitable liquids. Ignitable liquid (b) is an example of a blended product containing an aromatic product and a heavy petroleum distillate. Ignitable liquid (d) is a heavy petroleum distillate with limonene. There are many possible variations to the blended miscellaneous products.

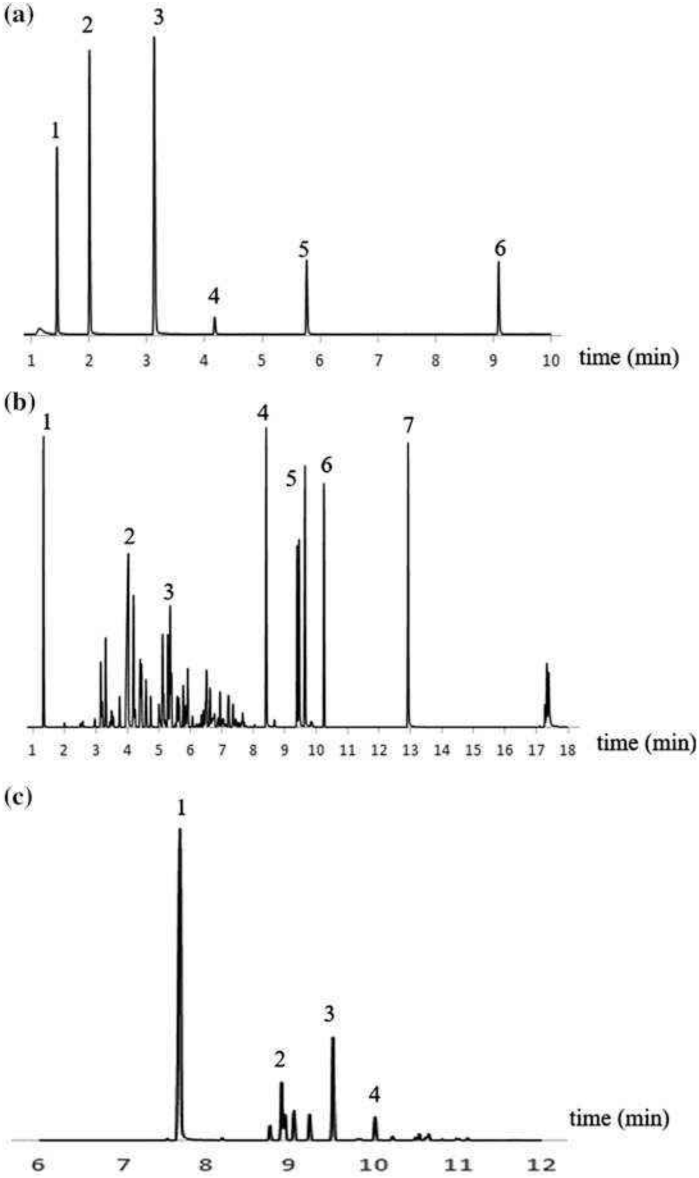


Fig. 5.24 Total ion chromatograms of three oxygenated solvents. Oxygenated solvent (**a**) contains only oxygenated compounds; (1) acetone, (2) 2-butanone, (3) 2-pentanone, (4) methyl isobutyl ketone, (5) butyl acetate, and (6) 3-ethoxy ethyl ester propionic acid. Oxygenated solvent (**b**) is a mixture of oxygenated compounds and a mixture of various other compounds; (1) ethanol, (2) methylcyclohexane, (3) 1,3-dimethylcyclohexane, (4) 1-butoxy-2-propanol, (5) dipropylene glycol methyl ether isomers, (6) limonene, and (7) 2-phenoxyethanol. Oxygenated solvent (**c**) contains a medium aromatic product with 2-butoxyethanol; (1) 2-butoxyethanol, (2) m, p-ethyltoluene, (3) 1,2,4-trimethylbenzene, and (4) 1,2,3-trimethylbenzene

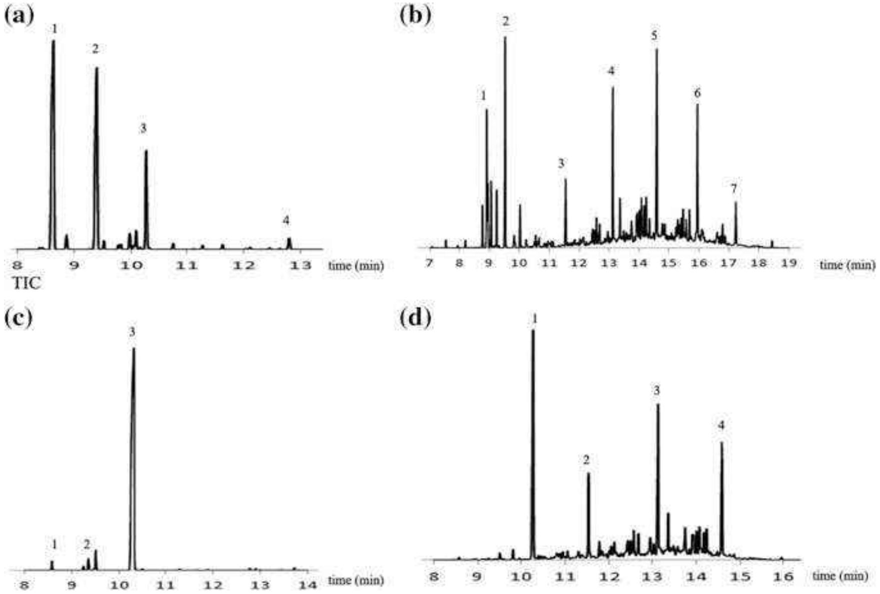


Fig. 5.25 Total ion chromatograms of four ignitable liquids categorized as miscellaneous. Ignitable liquids (**a**) and (**c**) are examples of nonpetroleum-based products: turpentine (**a**) and orange oil (**c**). Ignitable liquid (**a**) contains (1) alpha-pinene, (2) beta-pinene, (3) limonene, and (4) anisole. Ignitable liquid (**c**) contains (1) alpha-pinene, (2) beta-pinene, and (3) limonene. Ignitable liquid (**b**) is a blended product of an aromatic product and a heavy petroleum distillate that contains (1) m,p-ethyltoluene, (2) 1,2,4-trimethylbenzene, (3) n-undecane, (4) n-dodecane, (5) n-tridecane, (6) n-tetradecane, and (7) n-pentadecane. Ignitable liquid (**d**) is a medium petroleum distillate blended with limonene (1) that also contains; (2) n-undecane, (3) n-dodecane, and (4) n-tridecane

5.11 Conclusion

While it is important to recognize the classic representations of each ignitable liquid class, it is also important to recognize the range of variation within each of the classes. Investigations into determining if like petroleum products from various sources can be differentiated from one another have been conducted [15–23], but discussion of this type is beyond the scope of this text. Without knowledge of the variation in patterns and compositions within each class, an examiner can lead to an overly narrow characterization in classification. The importance of a broad, continually updated reference collection and ongoing communication between examiners is valuable.

5.12 Questions

1. What are the causes of variation seen within a class of ignitable liquids?
2. Which two classes of ignitable liquids have the most variation?
3. Explain why these two classes of ignitable liquids have the most variation.
4. What types of compounds vary in petroleum distillates?
5. Which class of ignitable liquids has the least variation?
6. Variation is observed in the chromatographic patterns of isoparaffinic products. Describe the observed variation and explain why.
7. What types of compounds vary the most in gasoline?
8. Explain how visually identical containers of a product can have widely divergent chemical content (e.g., petroleum distillate vs. isoparaffinic product)?

References

1. Where are the pipelines? http://www.api.org/oil-and-natural-gas/wells-to-consumer/transporting-oil-natural-gas/pipeline/where-are-the-pipelines. Accessed June 2018
2. ASTM Standard D4814–18c (2018) Standard specification for automotive spark-ignition engine fuel. ASTM International, West Conshohocken, PA, www.astm.org
3. EN 228:2008 Automotive fuels—Unleaded petrols—Requirements and test methods, https://www.cen.eu
4. Ethanol Production and Distribution, https://www.afdc.energy.gov/fuels/ethanol_production.html. Accessed June 2018
5. ASTM Standard E1618 (2014) Standard test method for ignitable liquid residues in extracts from fire debris samples by gas chromatography-mass spectrometry. ASTM International, West Conshohoken, PA, www.astm.org
6. Hetzel SS (2008) Survey of American (USA) Gasolines (2008). J Forensic Sci 60(Suppl 1): S197–206. https://doi.org/10.1111/1556-4029
7. Hendrikse J, Grutters M, Schäfer F (2015) Identifying ignitable liquids in fire debris: a guideline for forensic experts. Academic Press, Boston
8. Peschier L, Grutters M, Hendrikse J (2018) Using alkylate components for classifying gasoline in fire debris samples. J Forensic Sci 63:420–430. https://doi.org/10.1111/1556-4029.13563
9. Sandercock PML (2012). A Survey of Canadian Gasolines (2010). Can. Soc. Forensic Sci. J. Vol. 45:64-78
10. Baerncopf J, Hutches K (2014) A review of modern challenges in fire debris analysis. Forensic Sci Int 244:e12–e20
11. National Center for Forensic Science (2000) Ignitable liquids reference collection database. University of Central Florida. http://ilrc.ucf.edu/. Accessed 21 Mar 2018
12. Newman R, Gilbert M, Lothridge K (1998) Guide to ignitable liquids. CRC Press, New York
13. Sandercock PML (2007) A survey of Canadian gasolines (2004). Can Soc Forensic Sci J 40:105–130
14. National Center for Forensic Science (2006) International database of ignitable liquids. University of Central Florida, http://ncfs.ucf.edu/internationaldb Accessed June 2018
15. Sigman M, Williams M, Ivy R (2007) Individualization of gasoline samples by covariance mapping and gas chromatography/mass spectrometry. Anal Chem 79:3462–3468. https://doi.org/10.1021/ac062230n

16. Mann DC (1987) Comparison of automotive gasolines using capillary gas chromotography I: comparison methodology. J Forensic Sci 32:606–615
17. Mann DC (1987) Comparison of automotive gasolines using capillary gas chromotography II: Limitations of automotive gasoline comparisons in casework. J Forensic Sci 32:616–628
18. Barnes AT, Dolan JA, Kuk RJ, Siegel JA (2004) Comparison of gasolines using gas chromatography-mass spectrometry and target ion response. J Forensic Sci 49:1018–1023
19. Rankin JG, Harrington P (2012) Development and validation of a method for individualization of middle petroleum distillates and kerosene ignitable liquids. Rockville (MD): National Criminal Justice Reference Service; 2012 Dec. Document Number 240686, NIJ Award Number 2008-DN-BX-K146
20. ASTM Standard D3415 (2011) Standard practice for identification of waterborne oils. ASTM International, West Conshohocken, Pennsylvania, www.astm.org
21. Sandercock PML, Du Pasquier E (2003) Chemical fingerprinting of unevaporated automotive gasoline samples. Forensic Sci Int 134:1–10
22. Sandercock PML, Du Pasquier E (2004) Chemical fingerprinting of gasoline. 2. Comparison of unevaporated and evaporated automotive gasoline samples. Forensic Sci Int 140:43–59
23. Sandercock PML, Du Pasquier E (2004) Chemical fingerprinting of gasoline. Part 3. Comparison of unevaporated automotive gasoline samples from Australia and New Zealand. Forensic Sci Int 140:71–77

Mary R. Williams is a Researcher for the National Center for Forensic Science at the University of Central Florida. She administers fire debris and explosive-related databases. In addition, she specializes in fire debris analysis with published research in statistical methods of data interpretation.

Susan Seebode Hetzel is a Forensic Chemist in the forensic engineering firm S-E-A, Ltd., and specializes in fire debris analysis. Her research topics include the variation within gasoline and the persistence of ignitable liquids on recently sealed wood decking. She has also been active in the standard development process with both ASTM International and the Organization of Scientific Area Committees (OSAC) for Forensic Science.

Chapter 6
Microbial Degradation of Ignitable Liquids

Katherine Hutches

Learning Objectives

- Become familiar with the effects of microbial degradation may have on petroleum-based ignitable liquids.
- Understand the differences between weathering effects and microbial degradation.
- Understand possible methods of mitigating microbial activity, when these methods are needed, and the limitations of each method.
- Learn the effective use of comparison samples as applies to microbial activity.

While the discussion of **microbial degradation** is relatively new to fire debris chemists, it has long been a topic of interest for environmental researchers and the petroleum industry. As early as 1946, Claude ZoBell documented that hydrocarbons could be used by microorganisms as their single source of energy and carbon [1]. Initial interest from the environmental researchers focused on the effects of petroleum hydrocarbon mixtures on innate microbial populations, particularly in marine spillage events such as the sinking of the supertanker Torrey Canyon in 1967 [1]. Numerous microbes that can metabolize petroleum hydrocarbons were identified in a broad array of environmental studies. More recent studies have expanded the range of known hydrocarbon-consuming microorganisms to include a wide variety of bacteria and fungi, including the well-known *Penicillium* species and the notorious *Aspergillus Niger* [2]. The degradation efficacy that was observed in environmental research was exploited by petroleum researchers who sought to explore the opposite effect: how microbial populations could affect the composition of the petroleum products, rather than how the petroleum products affected the microbial communities already present. This led to the concept of **bioremediation**, which is a waste management technique that uses microbes to remove (consume) hydrocarbons from petroleum spills on land or water. As an example, bioremedi-

K. Hutches (✉)
Bureau of Alcohol, Tobacco, Firearms and Explosives, Walnut Creek, CA, USA

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_6

ation was used in the aftermath of the *Exxon Valdez* oil spill of 1989 to speed the degradation of the oil that came to shore [3]. The petroleum industry and environmental researchers determined that various factors affected the effectiveness of the bioremediation. Some common factors that were found to limit the effectiveness of biodegradation in the aquatic and terrestrial environments are low temperature, low concentration of mineral nutrients, insufficient oxygen, and the abundance and composition of the microbial community [4, 5]. Additionally, the effectiveness was influenced by the chemical composition and the concentration of available hydrocarbons [5].

6.1 Microbial Degradation and Fire Debris Analysis

In the last few decades, the fire debris community has become increasingly aware of the effects of microbial activity on fire debris evidence [6–10]. While the petroleum industry's focus is largely on *improving* the efficiency of the microbial degradation, the fire debris community's focus is on how the microbial degradation specifically affects the petroleum products in samples and, ultimately, the results of ignitable liquid analysis. Most of the samples that are known to be affected by microbial degradation are soil-based samples, though some degradation has also been observed on moldy building materials [11]. Considering the length of time generally required for samples to be collected, shipped, received, and processed at the laboratory in conjunction with the heavy application of water to fire scenes, it is not unreasonable to expect some level of microbial degradation to an ignitable liquid in soil samples or in samples with visibly obvious biological growth.

As discussed in Chap. 2, ignitable liquids are identified through pattern recognition and pattern comparison. The total ion chromatogram (TIC) and extracted ion profiles (EIPs) are examined for the presence of recognizable patterns of peaks that are common to various classes of petroleum products. For example, within a given cluster of compounds such as the C_3-alkylbenzenes, the ratios of peaks (**intragroup** ratios) remain relatively consistent from one petroleum product to another. This enables comparison of the patterns from an unknown debris sample to patterns from a known petroleum product, ultimately allowing identification of an ignitable liquid as appropriate. In addition to intragroup comparisons, the comparison of between-group (**intergroup**) ratios, such as the ratio of the C_2-alkylbenzenes to the C_3-alkylbenzenes, is important for the identification of an ignitable liquid.

When **weathering** of an ignitable liquid occurs, the most volatile components are lost in a predictable fashion, leaving the intragroup peak ratios relatively similar to those of the initial liquid (Fig. 6.1a, b). All of the peaks within a given cluster are still present, and the relative ratios of the compounds within most of the clusters remain largely unchanged. For example, the relative ratios of the three peaks in the C_2-alkylbenzene cluster (peaks 2–4) are maintained even after evaporation to approximately 75%. The ratios between groups, such as the ratio between the C_2-alkylbenzenes and the C_3-alkylbenzenes, will change in a predictable, reproducible

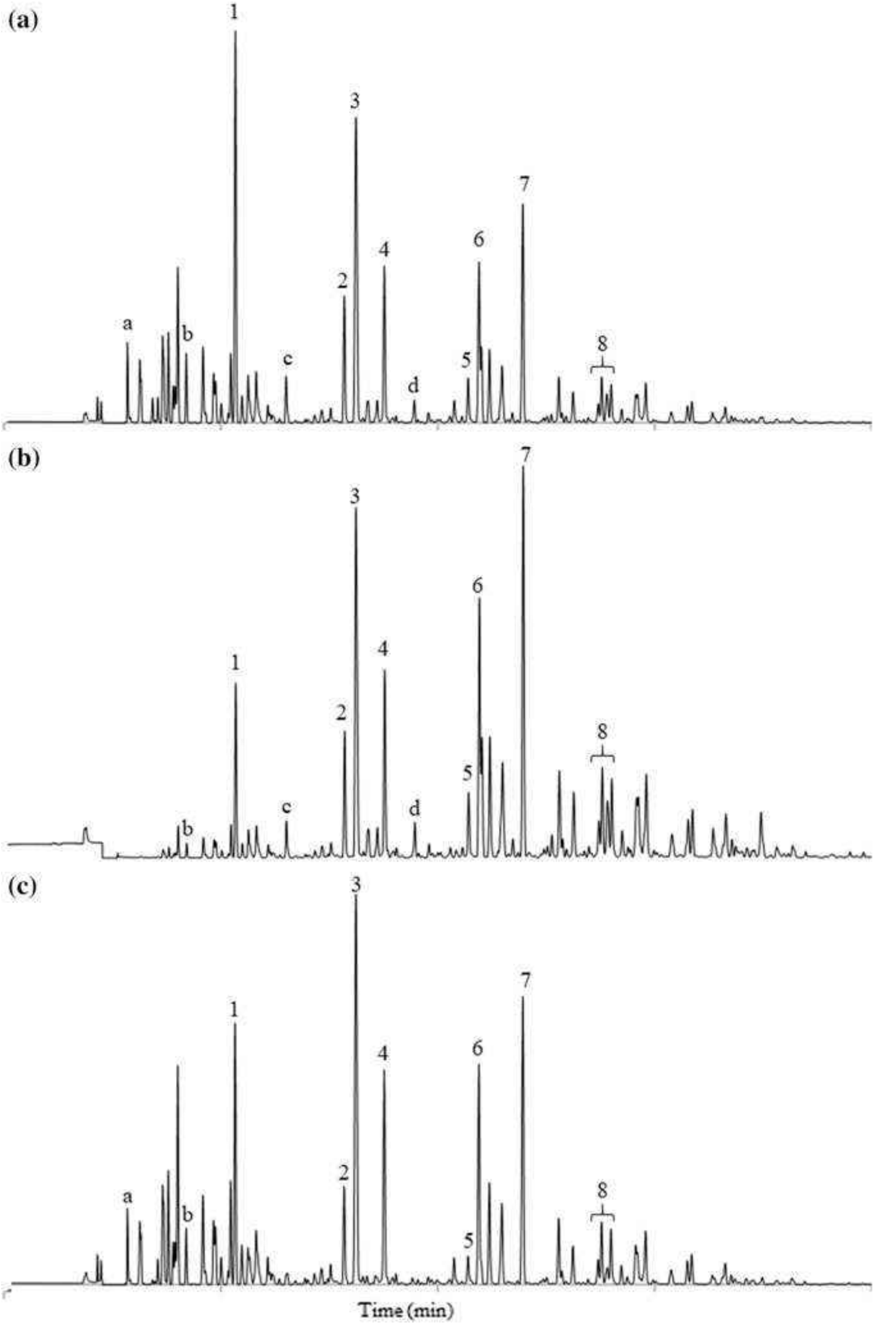


Fig. 6.1 Total ion chromatograms of **a** unevaporated (neat) gasoline; **b** 75% evaporated gasoline; **c** soil with added gasoline, stored at room temperature for two days

fashion, with the less volatile groups becoming more prominent as the more volatile groups are lost (see Chap. 5 for a more detailed discussion of weathering). As such, laboratories can generate reference ignitable liquids of different evaporation levels, such as 75 and 90% evaporated gasoline, to be used for pattern comparison as appropriate.

In microbial degradation, the diagnostic patterns that are used for identification of ignitable liquids are altered more unpredictably than with weathering. Instead of progressive losses of entire groups based on volatility, the losses are limited to single compounds within groups based on the preferences of the particular microbes that are present in a given sample. One of the most common classes targeted by microbial degradation is the normal alkanes (e.g., hexane, heptane) [1, 6, 9]. Another commonly degraded class of compounds in petroleum products is the monosubstituted alkylbenzenes (e.g., toluene, n-ethylbenzene, and n-propylbenzene).

Figures 6.1 and 6.2 depict the qualitative differences between evaporated gasoline and gasoline with minor microbial degradation. For ease of comparison, the C_6–C_9 normal alkanes are marked with letters and the major aromatic compounds are marked with numbers in both figures. In the evaporated gasoline (b), the diagnostic patterns are readily identifiable and intragroup ratios are maintained. Conversely, the intragroup ratios of compounds are beginning to change after only two days of exposure to soil (c). The monosubstituted aromatics (labeled 1, 2, and 5) are diminished relative to their neighbors (labeled 3, 4, and 6) in Fig. 6.1. Similarly, the normal alkanes (labeled a, b, c, d) are slightly diminished compared to their neighbors in Fig. 6.2.

At least two microbial species have been identified as likely being responsible for the microbial degradation of ignitable liquids in soil samples analyzed for ignitable liquids [7]. The first of the species identified in fire debris samples, *Pseudomonas putida*, has been credited with the consumption of monosubstituted alkylbenzenes. The second, *Pseudomonas fluorescens biovar III*, has been credited with the consumption of the normal alkanes. It is important to note that while each particular microbial species has a preferred type of chemical as a carbon source, the microbes may also adapt to consume whatever chemical compounds are available, provided that it has the proper metabolic pathways available [12]. This potential for variability by the same microbial species underscores the difficulty in predicting the types of losses that can be expected to occur due to microbial degradation.

Interestingly, the rate of loss for a given molecule is not only related to the chemical class to which it belongs (alkane, aromatic, etc.) and the microbial species involved, but also the length, extent, and even position of the branching of the molecule [10]. While normal alkanes are generally considered to be relatively easily consumed (depending on the microbial community), branched alkanes have shown to be more resilient against microbial degradation [4, 9]. Methyl branching is known to generally increase the resistance of a given alkane to microbial degradation [1]. To explain this effect, it is necessary to touch on how normal alkanes are

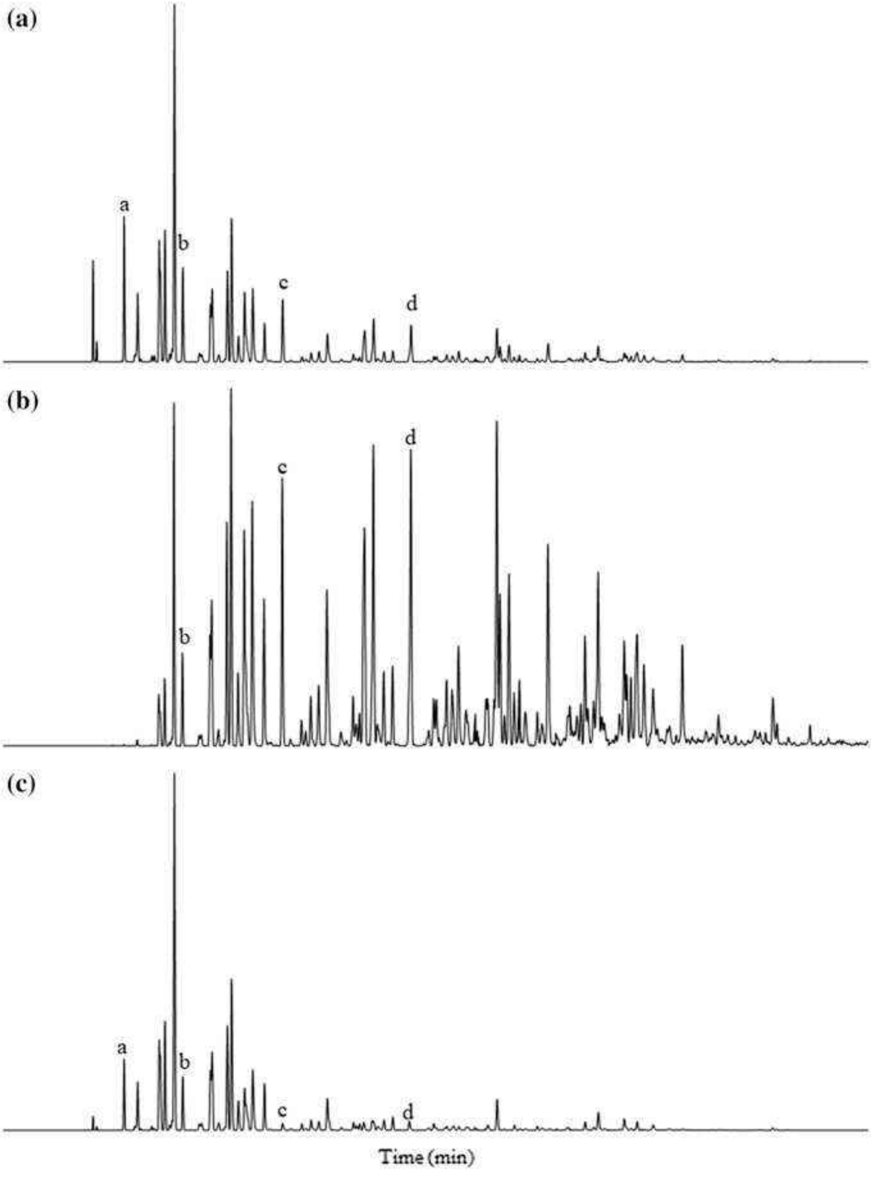


Fig. 6.2 Alkane extracted ion profiles of **a** unevaporated (neat) gasoline; **b** 75% evaporated gasoline; **c** soil with added gasoline, stored at room temperature for two days

metabolized by microbes. The degradation of normal alkanes generally begins with hydroxylation at one end, resulting in the formation of a primary alcohol, as shown in Fig. 6.3 [1, 4, 13]. This is one of the reasons that caution should be exercised

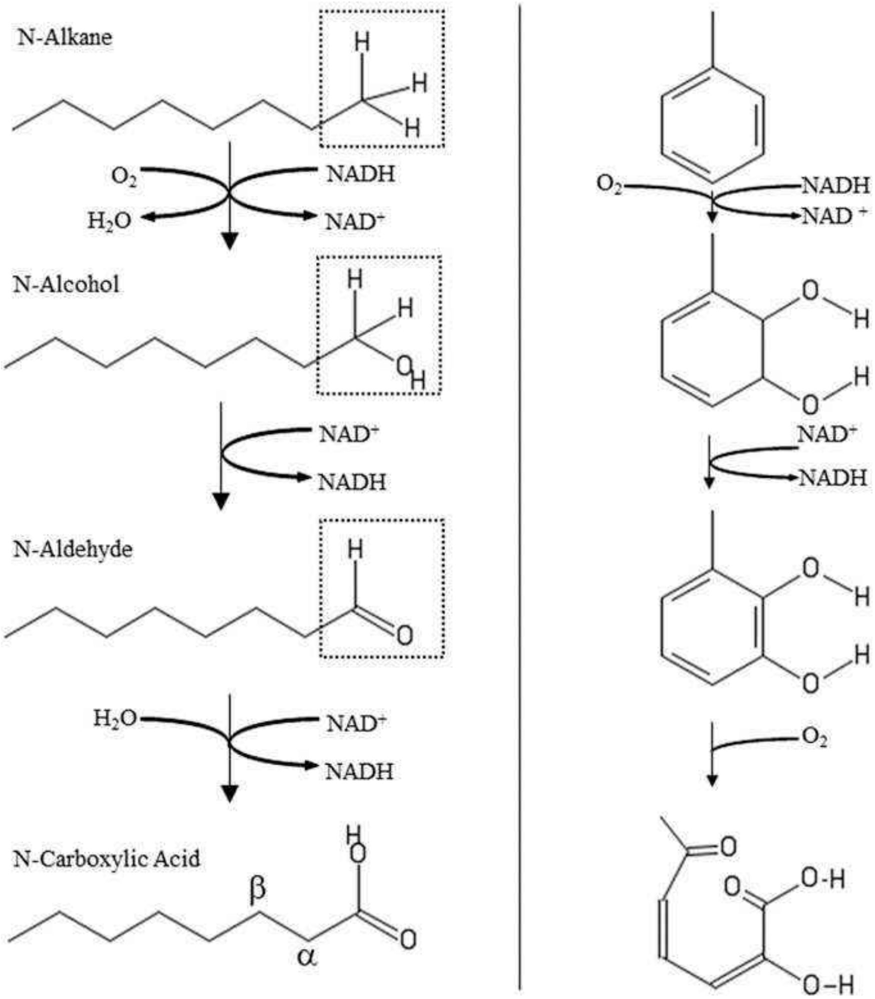


Fig. 6.3 Degradation mechanisms for aliphatic hydrocarbons (left) and aromatic hydrocarbons (right). Nicotinamide adenine dinucleotide (NAD^+) is a coenzyme that is necessary for both degradation mechanisms; NADH is the reduced form of NAD^+ [14]

when considering whether to report the presence of an alcohol in evidence—the alcohol may not have been added to the substrate by a human, but may be the result of microbial degradation or combustion/pyrolysis.

Further metabolism of the normal alkanes can result in oxidation to formaldehydes and carboxylic acids, which are not typically compounds of interest to the fire debris examiner. Aldehydes will also be readily apparent when the evidence is first opened in the form of a *very* unpleasant odor.

The next step in the metabolism of alkanes, not shown in Fig. 6.3, is β-oxidation of the carboxylic acid in Fig. 6.3. β-oxidation converts the α–β bond in the carboxylic acid to a double bond; this desaturation is greatly affected by the presence of branching in the β position and adjacent sites. As such, alkanes with branching are less likely to be degraded than normal alkanes, which do not have branching at these sites. The degradation of cyclic alkanes is similarly affected by the extent of branching and increasing chain length of alkyl substitution. Cyclic alkanes, however, are generally resistant to microbial degradation [15].

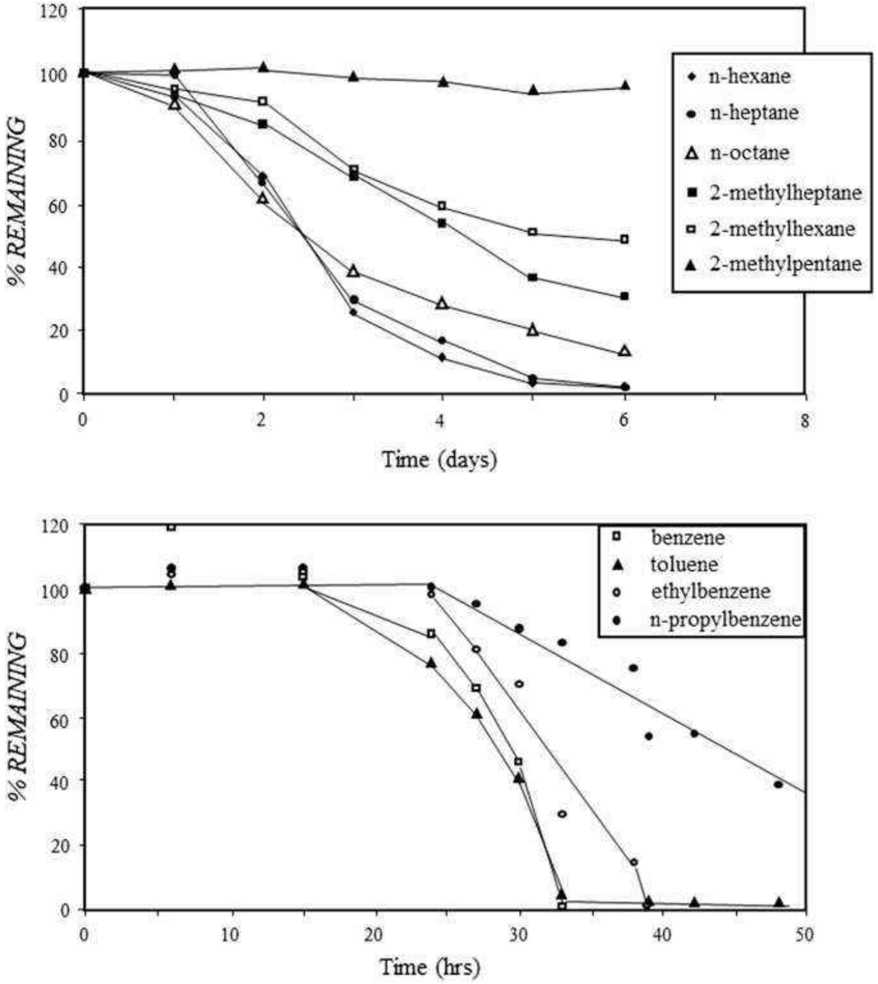


Fig. 6.4 (Top) Rates of consumption of aliphatic hydrocarbons in Shellite (light petroleum distillate) exposed to *P. fluoroscens biovar III*. (Bottom) Rates of consumption of aromatic hydrocarbons in gasoline exposed to *P. putida*. Adapted with permission from Kirkbride et al. [7]

The mechanism for the degradation of aromatic compounds is somewhat different. The degradation normally involves the addition of oxygen across one of the nominal double bonds, resulting in a *cis*-diol; the benzene-based diol is catechol [4, 16]. The aromatic ring is subsequently cleaved to form a dienedoic acid. The precise manner in which the diol is formed and the cleavage achieved varies widely between organisms. Regardless of the mechanism(s), however, increasing substitution has generally been observed to inhibit initial oxidation of the aromatic molecule, as was observed with aliphatic molecules. Kirkbride et al. observed that substitutions larger than a methyl group slowed the degradation of substituted aromatic compounds by *P. putida* [7]. As the length of the substitution increased, the rate of consumption decreased, as seen in Fig. 6.4. There is an interesting exception to the general rule about the extent of branching slowing the degradation of aromatic compounds. In the first fire debris paper regarding microbial degradation, Mann and Gresham also noticed that 1,2,4-trimethylbenzene was also consistently a target of microbial degradation, despite the extensive branching present in the alkyl group [6].

There was also an observable difference between the rates of degradation between the two species of microbes observed in Kirkbride's study, as seen in Fig. 6.4. The degradation of the aromatics by *P. putida* (plotted in hours) was much more rapid than the degradation of the aliphatics by *P. fluorescens biovar III* (plotted in days), with approximately 50% of C_1–C_3 singly substituted alkylbenzenes lost within 1–2 days of exposure, compared to the 2–3 days required for similar loss of C_5–C_8 normal alkanes.

6.2 Microbes and Ignitable Liquid Classification

Given the selective manner in which the microbes consume particular compounds within ignitable liquids, it is not surprising that different ignitable liquids are affected to different extents by microbial degradation.

The most commonly identified ignitable liquid in fire debris is gasoline [17], which is predominantly comprised of substituted aromatic compounds with lesser aliphatic content. As discussed in Chaps. 2 and 5, the aliphatic content can include variable abundances of normal, branched, and cyclic alkanes. When looking at a chromatogram, the aliphatic patterns are generally well below the abundance of the aromatic patterns, with the exception of the light end of unevaporated gasolines. As such, the effects of microbial degradation are generally most visible in the predominant aromatic patterns in the TIC.

In gasoline, the monosubstituted alkylbenzenes, which include toluene, ethylbenzene, and propylbenzene, are typically most affected by microbial degradation. Depending on the bacterial population, there may also be losses of the m-, p-xylenes, and 1,2,4-trimethylbenzene, but the monosubstituted alkylbenzenes are generally the first and most noticeable aromatic compounds to be lost [6, 9, 11, 18].

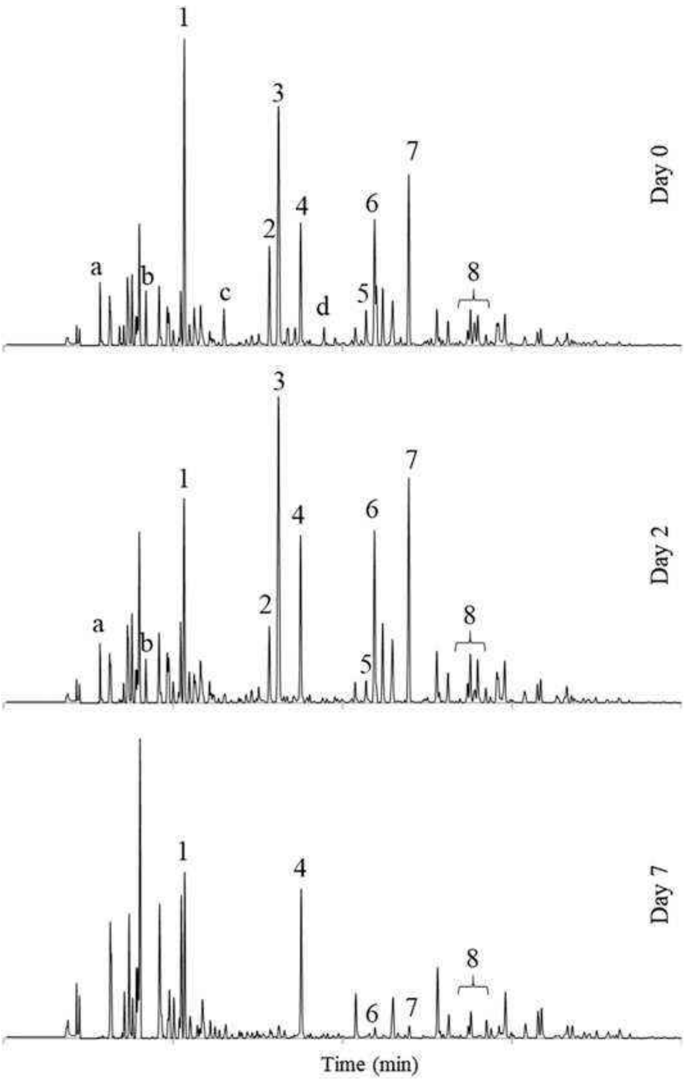


Fig. 6.5 Soil with added gasoline, stored at room temperature for zero days, two days, and seven days. A slight reduction in the monosubstituted alkylbenzenes is evident as early as two days after exposure

These losses will generally be visible in the TIC and in the aromatic EIP, as seen in Figs. 6.5 and 6.6. Similar trends have been observed with aromatic products [18].

More subtle losses may also be apparent in the alkane EIP, where the normal alkanes will be reduced from the neat liquid. Given the broad variability in alkane content between gasolines and the general lack of neat liquid samples for most cases, aliphatic losses may not be readily apparent.

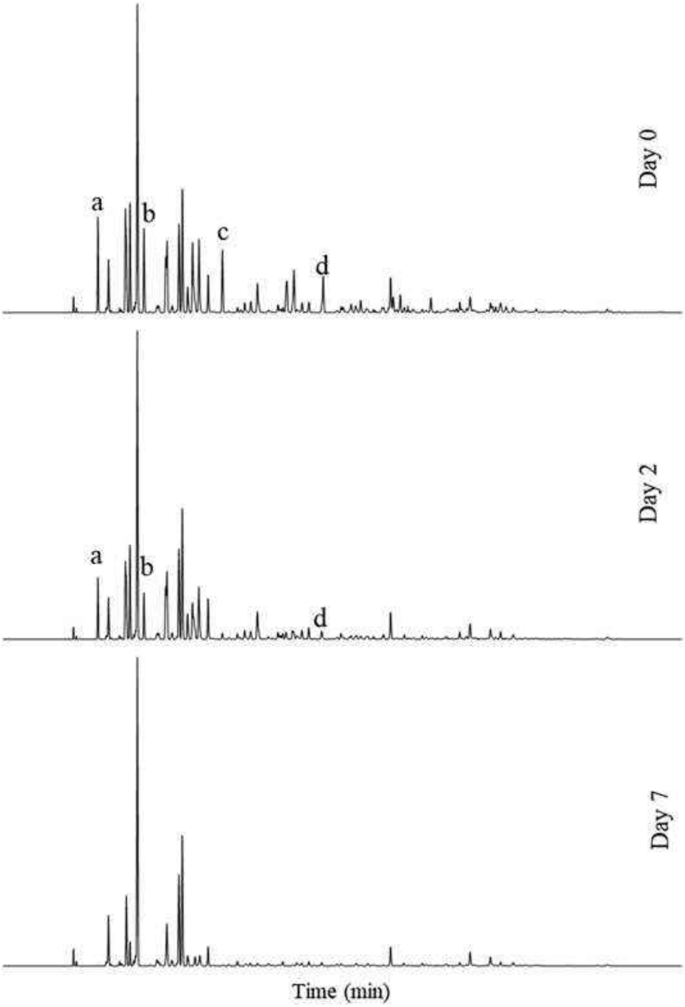


Fig. 6.6 Alkane EIP of soil with added gasoline, stored at room temperature for zero days, two days, and seven days

Petroleum distillates, particularly the medium- and heavy-range petroleum distillates, are also potentially susceptible to microbial degradation due to the predominate pattern of normal alkanes, as seen in Fig. 6.7. With the loss of the normal alkanes, all that is left may be a poorly resolved envelope of branched and cyclic alkanes—which are key indicators of a naphthenic–paraffinic product (along with a lack of aromatic content; see Chap. 2)—and may lead to a different classification than the original liquid. If the original distillate was not dearomatized, then the aromatic groups may or may not also be affected by the microbial degradation as discussed above for gasoline.

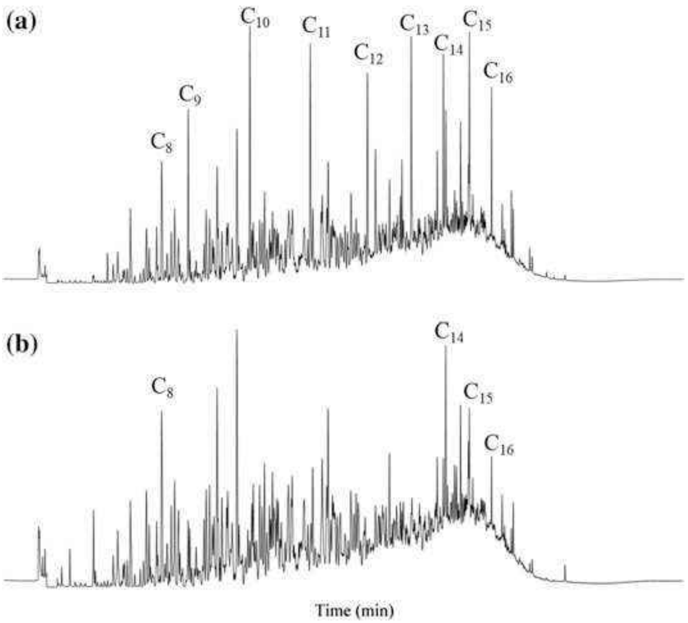


Fig. 6.7 Soil with added heavy petroleum distillate (HPD), stored at room temperature. **a** Zero-day exposure. **b** One-day exposure

Some petroleum-degrading microbes have been found to prefer a very narrow range of normal alkanes in petroleum distillates [19]. In Goodpaster and Turner's study, it was observed that the normal alkanes in the C_{11-15} range were degraded more severely than those in the C_{16-20} range [9]. It should be noted, however, that this trend was noted within heavy petroleum distillates, which have the most abundance normal alkanes in this range. In general, it is accepted that normal alkanes between C_{10} and C_{18} will be relatively easily degraded [4, 13]. There may also be a preference for the degradation of normal alkanes with even carbon numbers over those with odd carbon numbers, but this may not be readily observable in the TIC or alkane EIP [9, 20].

Contrary to what would be expected, normal alkane products appear to survive relatively intact despite exposure to microbial degradation [18]. A recent study showed that while there are slight changes in the ratios between peaks, the overall pattern was largely retained, despite ample normal alkane degradation of petroleum distillates prepared in the same soil. This may be due to the relatively higher concentration of the normal alkanes in the normal alkane product than in the distillates. As such, preferences by any bacteria present were not observable.

Naphthenic–paraffinic products appear to be generally unaffected by microbial degradation [10, 18]. Some naphthenic–paraffinic products will have a low abundance of normal alkanes. As expected, the normal alkanes are the first compounds to be lost by microbial degradation. The remaining compounds, however, are relatively resistant to degradation, which is not surprising given that naphthenic–paraffinic products are composed primarily of cyclic and branched alkanes, each of which is known to resist degradation.

Isoparaffinic products show slightly more degradation than naphthenic–paraffinic products [18]. The long-chain, less branched alkanes are lost more rapidly than shorter chains of similar branching, which is predictable given the monoterminal hydroxylation step shown in Fig. 6.3. The long-chain alkanes may be branched at one end, but with increasing length the opposite end appears more similar to a normal alkane, potentially rendering it vulnerable to microbial degradation. While each of these products suffers some loss of the less-substituted alkanes, such as 2- and 3-methylalkanes, the losses are much less drastic than the losses observed in gasoline and petroleum distillates.

6.3 Other Factors Affecting Microbial Degradation

While microbial degradation may be a concern in biologically active samples such as soil or moldy building materials, there are steps that can be taken to mitigate this microbial degradation. By understanding factors that can affect microbial degradation, investigators and examiners can potentially slow the degradation of ignitable liquids.

6.3.1 Mitigating Microbial Degradation

One of the main factors affecting the rate of microbial degradation of petroleum-based ignitable liquids is temperature. While degradation of petroleum products *can* occur at sub-zero temperatures, the rate of degradation at low temperatures is generally far slower than the rate of degradation at higher temperatures [4, 6]. As such, laboratories should recommend that soil and moldy evidence be frozen or chilled when not actively being transported to minimize further microbial activity. Once the samples are received at the laboratory, they should be chilled unless they are being immediately analyzed to help prevent any further degradation. Figure 6.8 demonstrates the effectiveness of chilling soil samples; in the unrefrigerated samples, there are losses to the singly substituted alkylbenzenes (*) beginning on Day 2, and characteristic patterns are lost by Day 7 when unrefrigerated.

Interestingly, this temperature trend does not directly translate to the degradation observed in soil based on season. In a study involving three separate soil types, it was observed that more severe degradation occurred during the winter months than in the summer months [21]. While this seems counterintuitive, it is important to remember that there is an upper temperature limit for bacteria to thrive. In summer, this limit was exceeded for most of the bacteria. Additionally, during the summer that this study was conducted, it was unusually dry, and moisture is an essential

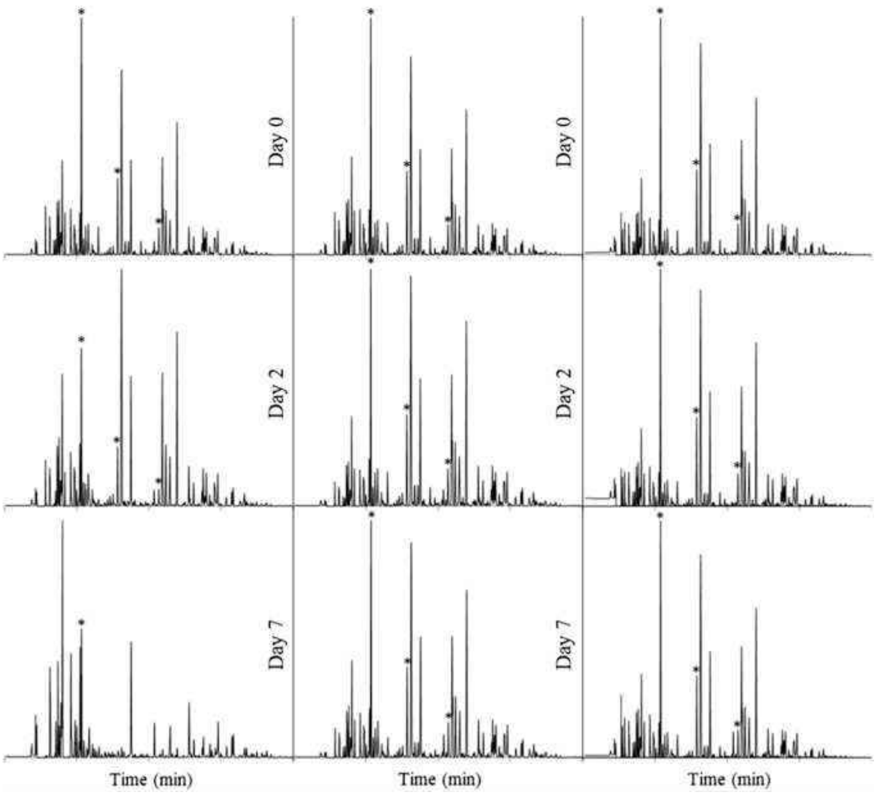


Fig. 6.8 Soil with added gasoline stored at room temperature (left), refrigerated (middle), and with oxygen-absorbing pouch (right). Monosubstituted alkylbenzenes (*)

component in microbial activity. No particular trends specific to petroleum degradation have been published, however. Finally, other nutrients in the soil such as nitrates were found to vary with season, either due to the addition of commercial fertilizers or the breakdown of nearby organic material. The presence or absence of these nutrients can also play a role in the activity of microbes.

Another factor affecting microbial activity is the presence or absence of oxygen. All previous discussion has involved aerobic degradation, which is degradation in the presence of oxygen. Even a sealed can, which is common with fire debris evidence, is an aerobic environment due to the amount of oxygen present within the can at the time of sealing. An anaerobic environment is an environment with little to no oxygen. While anaerobic degradation of petroleum products can occur [15, 19, 22, 23], the rate and extent of the degradation are less than in aerobic environments and depend greatly on the availability of certain nutrients, such as nitrates and sulfates [4, 5, 22]. Research has been conducted to determine if removal of oxygen would significantly slow microbial degradation in soil samples submitted for ignitable liquid analysis, as an alternative to chilling the samples [24]. Initial testing used commercially available carbon dioxide cartridges to displace the oxygen, but it was insufficient to prevent microbial degradation and carried the risk of contamination from the cartridge itself. Limited successful tests with oxygen-absorbing pouches, however, suggest a potential viable method for mitigating microbial degradation if cold temperatures are not available (Fig. 6.8).

Another method of mitigation that has been presented is the application of a pre-made solution of triclosan, a known antimicrobial agent in a variety of household products [25]. This treatment requires extensive application of 1.8% triclosan in 0.1 M NaOH, at a ratio of approximately 3 milliliters of solution for every 5 grams of soil. While this method was proven effective at negating microbial activity in soil samples, there are also concerns regarding potential contamination and corrosion, especially because there will be extensive moisture in metal cans for extended periods. Additionally, this treatment method requires an extensive volume of pre-made solution, which fire investigators will likely have prepared by a laboratory rather than having on-hand. Furthermore, triclosan has already been banned from consumer soaps and antiseptic products in the USA, following a ruling by the Federal Drug Administration that triclosan was not generally recognized as safe and effective, making purchase of this compound relatively difficult [26, 27].

6.3.2 Variation in Soils

Different soils can have drastically different rates and specificities of degradation of a given ignitable liquid, likely due to differences in the microbial communities, available nutrients, moisture content, etc. For example, Fig. 6.9 shows a visible difference in the degradation rates and patterns of gasoline on two different soils. The broad variability between the degradation rates and even preferential degradation of various soils emphasizes the need for comparison soil samples when attempting to evaluate questioned soil samples. While general trends have been described above, the simplest way to determine whether microbial degradation could be responsible for the pattern observed in a case sample is to spike a small portion of a comparison soil sample with ignitable liquid in an attempt to recreate the pattern.

Comparison Soil Samples

Soil samples should be collected at the same time as the questioned soil samples. If microbial degradation is suspected, a subsection of the **comparison soil** sample can be spiked with an aliquot of a reference of the suspected original ignitable liquid class and left at room temperature for an extended period of time (depending on the circumstances of the case). The resulting pattern can be compared to the questioned sample to see if an identification can be made.

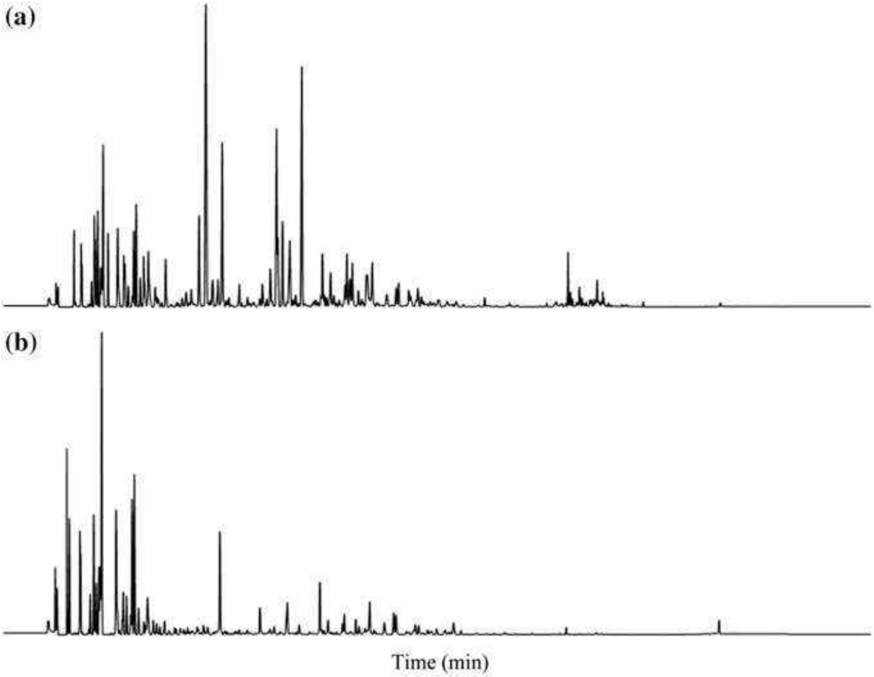


Fig. 6.9 Two different gasoline-spiked soils, three weeks after exposure. The topsoil has visible degradation of toluene and ethylbenzene, but the C_3- and C_4-alkylbenzene groups are unaffected and could easily be identified as gasoline. The bottom soil has extensive degradation with little indication of gasoline ever having been present

The comparison soil needs to be roughly similar soil. In regions with a great deal of variability in soil types within short distances, or in areas with mixed landscaping, it is very important that the soil is collected in a proximal area and is, at a minimum, visually comparable in texture and color. If a sample is collected from a planted flowerbed with clearly amended soil, a comparison sample should not be taken from the rather rocky, clearly unamended soil across the yard. Instead, it should be taken from another area of the amended flowerbed that is near enough to be similar in composition, yet far enough away (if possible) that it is not reasonably suspected to contain an ignitable liquid. Since the rate of microbial degradation within soil samples even varies by the season in which the samples were taken [21], comparison samples should be taken at the same time as the questioned samples.

While these general trends have been repeatedly observed in research environments, it is important to note that casework samples may have different microbial communities. The method used to enrich the bacterial cultures in Kirkbride's study is known to encourage the growth of *Pseudomonas* varieties, at the potential expense of other microorganisms [7]. Depending on the relative microbial loads of the two known *Pseudomonas* and other microbes in a given sample, the degradation rates and effects observed in research could be completely different from those observed in casework.

Recently, the use of microbes as a bioremediation agent has been translated into a novel firefighting foam. The idea behind the new foam is that after the fire is suppressed, the microbes in the foam can then reduce the environmentally harmful footprint of the fire by digesting any remaining 'hydrocarbons.' This commercially available microbially active firefighting foam uses a mixture of three different *Bacillus* microbes to achieve degradation of 'hydrocarbons,' which potentially includes petroleum products [28]. Of the three spore-producing microbes used in the foam, only one, *Bacillus subtilis*, is mentioned in environmental literature as a degradation agent [29, 30]. The other two microbes, *Bacillus licheniformis* and *Bacillus polymyxa*, are known for improving oil recovery, but may not be involved in the immediate degradation of petroleum products. To date, there have been no studies published regarding the degradation of ignitable liquids with the use of this new foam.

6.4 Questions

1. In what type of evidence would ignitable liquids be expected to undergo microbial degradation?
2. Why is considering microbial degradation an important part of fire debris analysis?
3. What types of compounds are the most affected by microbial degradation? Which ignitable liquid classifications?
4. What steps can be taken to mitigate microbial degradation? What are the benefits and limitations of each?
5. What is the difference between weathering and microbial degradation?

References

1. Atlas R (1981) Microbial degradation of petroleum hydrocarbons: an environmental perspective. Microbiol Rev 45(1):180–209
2. Okoro CC (2008) Biodegradation of hydrocarbons in untreated produce water using pure fungal cultures. AfrJ of Microbiol Res 2(8):217–223
3. Atlas RM, Hazen TC (2011) Oil biodegradation and bioremediation: a tale of the two worst spills in U.S. history. Environ Sci Tech 45(16):6709–6715. https://doi.org/10.1021/es2013227
4. Atlas R, Burtha R (1998) Microbial ecology: fundamentals and applications, 4th edn. Benjamin/Cummings Science Publishing, Menlo Park
5. Leahy JG, Colwell RR (1990) Microbial degradation of hydrocarbons in the environment. Microbiol Mol Biol 54(3):305–315. https://doi.org/10.1016/j.forc.2018.03.001

6. Mann D, Gresham W (1990) Microbial degradation of gasoline in soil. J For Sci 35(4):913–923. https://doi.org/10.1520/JFS12904J
7. Kirkbride KP, Yap SM, Andrews S, Pigou PE, Klass G, Dinan AC, Peddie FL (1992) Microbial degradation of petroleum hydrocarbons: implications for arson residue analysis. J For Sci 37(6):1585–1599. https://doi.org/10.1520/JFS13349J
8. Chalmers D, Yan S, Cassista A, Hrynchuk R, Sandercock PML (2001) Degradation of gasoline, barbecue starter fluid, and diesel fuel by microbial action in soil. Can Soc For Sci J 34(2):49–62. https://doi.org/10.1080/00085030.2001.10757517
9. Turner D, Goodpaster J (2009) The effects of microbial degradation on ignitable liquids. Anal Bioanal Chem 394(1):363–371. https://doi.org/10.1007/s00216-009-2617-z
10. Turner D, Goodpaster J (2011) The effect of microbial degradation on the chromatographic profiles of tiki torch fuel, lamp oil, and turpentine. J For Sci 56(4):984–987. https://doi.org/10.1111/j.1556-4029.2011.01749.x
11. Hutches K (2013) Microbial degradation of ignitable liquids on building materials. For Sci Int 232(1–3):e38–e41. https://doi.org/10.1016/j.forsciint.2013.08.006
12. Todar K (2008–2012) Regulation and control of metabolism in bacteria. http://textbookofbacteriology.net/regulation.html. Accessed 8 July 2018
13. White D (1999) The physiology and biochemistry of prokaryotes. Oxford University Press, New York
14. Mathews CK, van Holde KE, Ahern K (2000) Biochemistry, 3rd edn. Addison Wesley Longman Inc, San Francisco
15. Van Hamme J, Singh A, Ward O (2003) Recent advances in petroleum microbiology. MicrobiolMol Biol Rev 67(4):503–549. https://doi.org/10.1128/MMBR.67.4.503-549.2003
16. Madigan ME, Martinko J, Parker J (2000) Brock biology of microorganisms, 9th edn. Prentice Hall, Upper Saddle River
17. Sandercock PML (2017) A survey of fire debris casework in Canada, 2011–2016. Can Soc Forensic Sci J. https://doi.org/10.1080/00085030.2017.1380979
18. Turner D, Williams M, Sigman M, Goodpaster J (2018) A comprehensive study of the alteration of ignitable liquids by weathering and microbial degradation. J For Sci 63(1):58–65. https://doi.org/10.1111/1556-4029.13527
19. Spormann A, Widdel F (2000) Metabolism of alkylbenzenes, alkanes, and other hydrocarbons in anaerobic bacteria. Biodegradation 11:85–105. https://doi.org/10.1023/A:1011122631799
20. Kindell J, Williams M, Sigman M (2017) Biodegradation of representative ignitable liquid components in soil. For Chem 6:19–27. https://doi.org/10.1016/j.forc.2017.09.003
21. Turner D, Pichtel J, McKillip J, Goodpaster J (2013) Development of a sampling system to stabilize ignitable liquid residues in fire debris. NCJRS Photocopy Services, Rockville. Retrieved from https://www.ncjrs.gov/pdffiles1/nij/grants/242146.pdf
22. Grishchenkov VG, Tonsend RT, McDonald TJ, Autenrieth RL, Bonner JS, Boronin AM (2000) Degradation of petroleum hydrocarbons by facultative anaerobic bacteria under aerobic and anaerobic conditions. Process Biochem 35:889–896. https://doi.org/10.1016/S0032-9592(99)00145-4
23. Chakraborty R, Coates J (2004) Anaerobic degradation of monoaromatic hydrocarbons. Appl Microbiol Biotechnol 64(4):437–446. https://doi.org/10.1007/s00253-003-1526-x
24. Hutches K, Hoult J (2018) Practical methods for mitigating microbial degradation of ignitable liquids in soil samples. For Chem 8:95–103. https://doi.org/10.1016/j.forc.2018.03.001
25. Turner DA, Goodpaster JV (2014) Preserving ignitable liquid residues on soil using Triclosan as an anti-microbial agent. For Sci Int 239:86–91. https://doi.org/10.1016/j.forsciint.2014.03.011
26. Federal Drug Administration, Safety and Effectiveness of Health Care Antiseptics; Topical antimicrobial drug products for over-the-counter human use; 82 Federal Register 60474, 20 Dec 2017
27. Hogue Cheryl (2018) US FDA halts use of triclosan in health care antiseptics. Chem Eng News 96(1):15–15
28. Cox CS (1999) United States Patent No. 5942552

29. Nwaogu LA, Onyeze GOC, Nwabueze RN (2008) Degradation of diesel oil in a polluted soil using Bacillus subtilis. AfrJ Biotechnol 7(12):1939–1943. https://doi.org/10.5897/AJB07.889
30. Queiroga CL, Nascimento LR, Serra GE (2003) Evaluation of paraffins biodegradation and biosurfactant production by Bacillus subtilis in the presence of crude oil. Braz J Microbiol 34 (4). https://doi.org/10.1590/s1517-83822003000400006

Dr. Katherine Hutches was a forensic chemist in the Bureau of Alcohol, Tobacco, Firearms, and Explosives until her departure in the summer of 2019. She specialized in fire debris and explosive analysis, and her published research topics include novel analytical methods, gasoline-chlorinator mixtures, and microbial degradation in moldy building materials.

Chapter 7
Introduction to the Forensic Analysis of Intact Explosives

H. E. Hutson and E. McGee

Learning Objectives

- Understand what explosives are and how they are classified.
- Understand how explosives are properly submitted to the forensic laboratory.
- Understand how explosives are safely handled, analyzed, identified, and reported.

7.1 Introduction

An **explosive** is a substance or a mixture of substances that is capable of producing an explosion by its own energy. An **explosion** is a sudden and violent release of energy in the form of pressure (gaseous products), light, heat, and sound. Colloquially, this term is used to describe the violent shattering or blowing apart of something. Explosions can be considered as one of four distinct types: mechanical, nuclear, electrical and, most pertinent to the explosives in this chapter, chemical. **Chemical explosions** are the result of a rapid self-sustaining exothermic chemical reaction.

Content includes material subject to © Crown copyright (2018), Dstl. This material is licensed under the terms of the Open Government Licence except where otherwise stated. To view this licence, visit http://www.nationalarchives.gov.uk/doc/open-government-licence/version/3 or write to the Information Policy Team, The National Archives, Kew, London TW9 4DU, or email: psi@nationalarchives.gsi.gov.uk

H. E. Hutson (✉)
Defence Science and Technology Laboratory, Salisbury, Wiltshire, UK
e-mail: hehutson@mail.dstl.gov.uk

E. McGee
Centre of Forensic Sciences, Toronto, ON, Canada
e-mail: eamonn.mcgee@ontario.ca

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_7

Explosives are widely used throughout the world legally in different industries such as quarrying, mining, engineering, and demolition. They are also used by law enforcement and the military. Unfortunately, explosives are also used for nefarious purposes, resulting in the submission of explosives to forensic laboratories for identification.

An **intact explosive** (sometimes referred to as **bulk explosive**) can generally be thought of as unreacted energetic material, e.g., an intact stick of dynamite or the contents of an unfired firework. The characteristic appearance will not have changed significantly and the original ingredients will be present, though some may have degraded over time. Post-blast explosives will be discussed in Chap. 8.

Legislation varies across jurisdictions, but the basic requirements for every forensic laboratory analyzing explosives will not differ greatly. The courts will require confirmation that the substance recovered is indeed an explosive and a definitive confirmation of the identity. The laboratory can also perform chemical comparisons of explosives from different locations such as the crime scene and a suspect's residence and vehicle. Depending on the jurisdiction and the defined parameters of the examiner's duties, the origins, characteristics, and effects of the quantity and type of explosive may also be included in a report. The report will not include assessment of the intent of the perpetrator or defendant, as the intent is ultimately for the courts to decide, not the expert.

The last decade has seen more submissions of homemade explosives (HMEs) and related improvised explosive devices (IEDs) due to increased terrorist activity and experimenters. Homemade explosives, also known as **improvised explosives**, are used by lone wolves and organized groups to spread terror throughout the world. They are also synthesized by amateur chemists for experimentation, the legality of which varies across jurisdictions and countries. This means that laboratories may be regularly called upon to identify potential precursor chemicals for explosives manufacture and comment on the effectiveness of recipes for explosives found in a suspect's possession. Explosives examiners may also describe and report on device components such as containers, added enhancements, initiators, batteries, wires, switches, timers, and other electronics from IEDs, which are discussed in detail in Chap. 9. The question of whether the device would have functioned or not must be addressed, but different agencies may assign this assessment to different personnel.

Examiners may also be sent to scenes where presumptive testing is needed or to help with proper evidence collection. Presumptive testing, while not as conclusive as testing at the laboratory, can assist the investigation and increase the safety of those examining the crime scene, particularly where the manufacture of explosives and/or IEDs is suspected. Early indications of the identity of explosives on scene can also assist in the prioritization of any potential exhibits when submitted to the laboratory.

7.2 General Classification of Explosives

There are a wide variety of explosive substances [1–3], but these substances can be divided into two general categories based on their method and rate of reaction propagation: low explosives and high explosives. Upon initiation, **low explosives** undergo **deflagration**, a process in which each particle of the powder transfers heat to its immediate surroundings, resulting in a rapid rate of particle-to-particle burning with the production of hot gases and smoke. The reaction through the substance occurs at a rate less than the speed of sound in the unreacted material, which defines the material as a low explosive. **High explosives** undergo **detonation**, a process in which a shock wave moves through the unreacted material at a rate faster than the speed of sound. Commercial low explosives are commonly seen in casework, while commercial high explosives are more highly regulated and monitored than in the past, and are seen less frequently than before.

7.2.1 Low Explosives

Low explosives, with the exception of smokeless powders, are typically mechanical mixtures of oxidizers and fuels in powder form.

The commercial uses of low explosives can be generally divided into two categories: **propellants**, such as are used to propel a bullet from a gun, or **pyrotechnics**, such as are used in the fireworks and theatrical (stage) pyrotechnics industry [4, 5]. Examples are shown in Fig. 7.1. Some low explosives, particularly those that are homemade, such as potassium nitrate/sugar mixtures, will not fall neatly into one of these categories, but can generally be described as oxidizer/fuel mixtures.

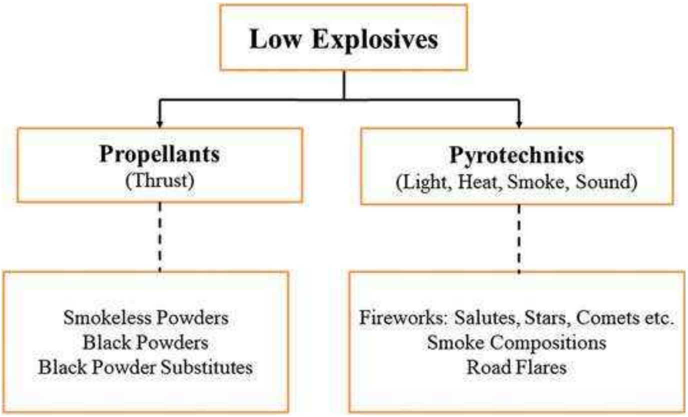


Fig. 7.1 Uses and examples of low explosives. © Crown copyright, Dstl

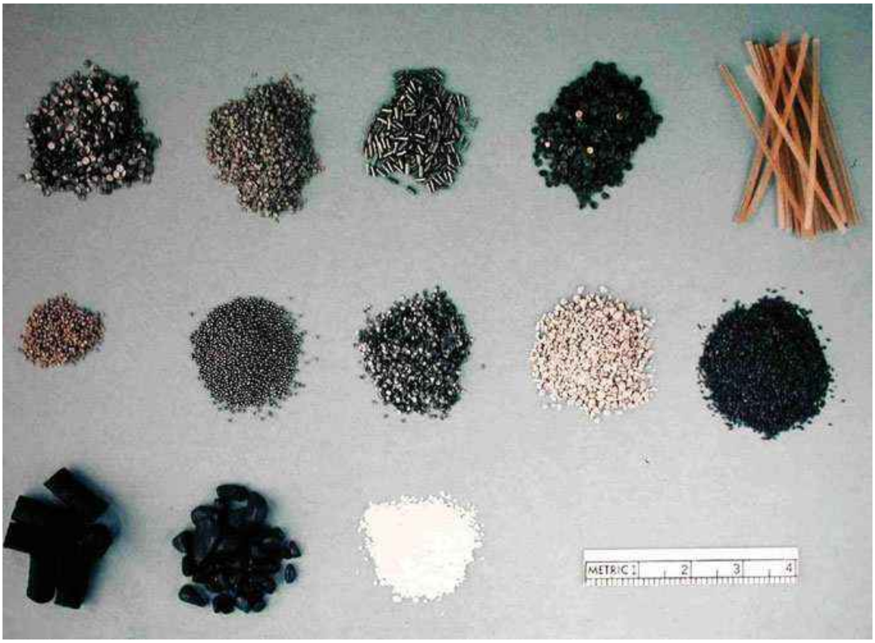


Fig. 7.2 Low explosives come in a range of morphologies and colors. © Crown copyright, Dstl

As can be seen in Fig. 7.2, low explosives can have many appearances, including white solids, black particles, gray powders, and firearms propellants in many shapes, sizes, and colors.

The speed of reaction through a low explosive is increased by the degree of confinement. Unconfined low explosive burns at a speed considerably slower than low explosive confined within a paper tube, which burns more slowly than low explosive confined within a metal pipe. If low explosives are suitably confined, the resulting speed of reaction increases and this can often result in a loud report (a bang). The rate of reaction is also affected by how intimately the fuel(s) and oxidizer(s) are mixed.

Propellant powders, including **black powders**, **black powder substitutes**, and **smokeless powders**, are historically the explosives most frequently submitted to most forensic laboratories. They are used in muzzleloading and cartridge firearms by ‘reloaders’ including hunters and gun enthusiasts and in historical re-enactments and are widely available for purchase in retail outlets.

Black powder is widely regarded as the oldest chemical explosive, dating back to around the seventh century [6]. The appearance can range from a fine powder to the angular granular material shown in Fig. 7.3. Commercial black powder consists of a mixture of potassium nitrate (oxidizer), charcoal (fuel), and sulfur (fuel and tinder to promote burning). Black powder is produced as a homogenous mixture in a range of grain sizes for different applications. The finer the grain size, the faster

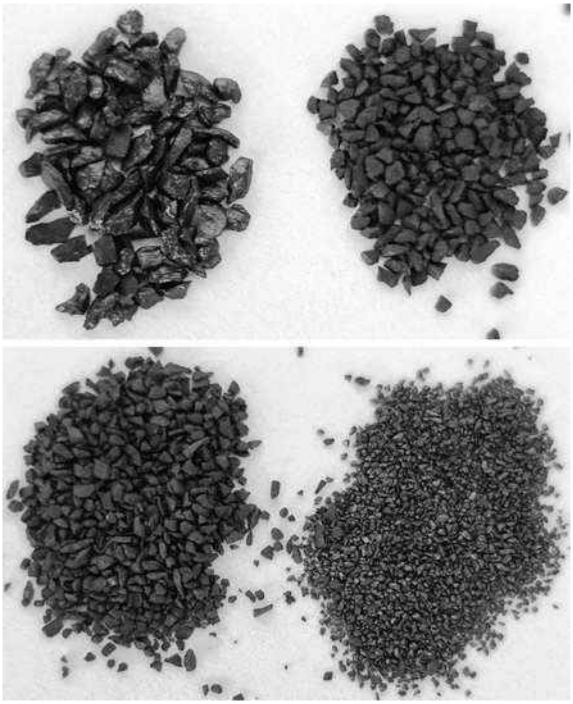


Fig. 7.3 Black powder is sold in different grain sizes. Left to right, Fg and FFg (top row) and FFFg and FFFFg (bottom row). © Crown copyright, Dstl

the burn. Coarse grains are designated Fg, medium FFg, fine FFFg, and very fine FFFFg as shown in Fig. 7.3. The grain size can be a useful physical property when comparing powders.

Pyrotechnic devices such as commercial fireworks and stage pyrotechnics use the propelling power of black powder as well. For example, black powder is commonly used to produce hot gases which are channeled from the base of a rocket to propel it into the air. Black powder is also used as the lifting charge within aerial shells fired from mortar tubes. Low explosives such as black powder are also used as the means to transmit flame in various fuses, which are discussed further in Chap. 9.

Examiners may also encounter homemade black powder, which consists of the same compounds as commercial black powder, but is generally very inhomogeneous with coarse particles that can be relatively easily separated for analysis.

Black powder substitutes, such as the ones shown in Fig. 7.4, offer some advantages over black powder for consumers; they are less sensitive to accidental initiation, and therefore, safer to use and less residue is produced after burning. The substitutes contain potassium nitrate and potassium perchlorate as oxidizers with a variety of fuels and other additives including sodium benzoate, sulfur, dicyandiamide, and ascorbic acid. A number of brands are on the market, each with their own particular composition.

Two of the most well-known and encountered substitutes are Pyrodex® and Triple Seven®, both of which look like gray aggregates with white inclusions when

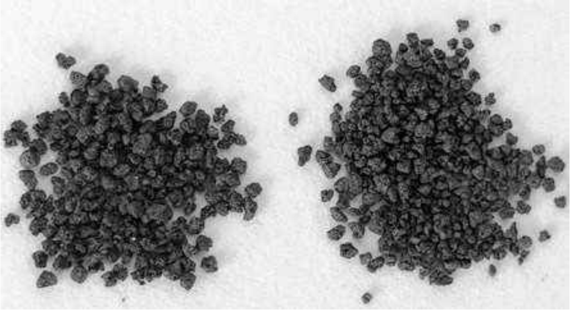


Fig. 7.4 Triple Seven (left) and Pyrodex® (right) are black powder substitutes. Grain sizes FFg are shown here. © Crown copyright, Dstl

magnified. Both contain the oxidizers potassium nitrate and potassium perchlorate. Pyrodex® additionally contains sulfur, sodium benzoate, and dicyandiamide (DCDA), whereas Triple Seven® lacks sulfur but contains 3-nitrobenzoic acid [7].

Some substitutes, such as BlackMZ™, contain ascorbic acid as the fuel source, typically with potassium nitrate and potassium perchlorate as oxidizers. Propellants utilizing an ascorbic acid fuel source generally do not contain sulfur [8].

Black powder substitutes also come in pellet form for muzzleloading. The pellets are typically gray, black, blue, or white in color and have a hole through the center. White Hots®, shown in Fig. 7.5, is an interesting example of a pelletized black powder substitute, which contains potassium nitrate, potassium perchlorate, sodium benzoate (fuel), and dextrin (binder and fuel).

Smokeless powder was developed in the late nineteenth century as the original substitute for black powder [6, 9], but should not be confused with the black powder substitutes described above, as it is physically and chemically very different from them. While not entirely free of smoke, the amount of smoke emitted on ignition is minimal because the majority of products formed are gaseous and colorless, which gives a much cleaner burn than black powder.

Smokeless powders come in many different morphologies and colors (see Fig. 7.6) and intact grains, sometimes called flakes, particles, or kernels, which are

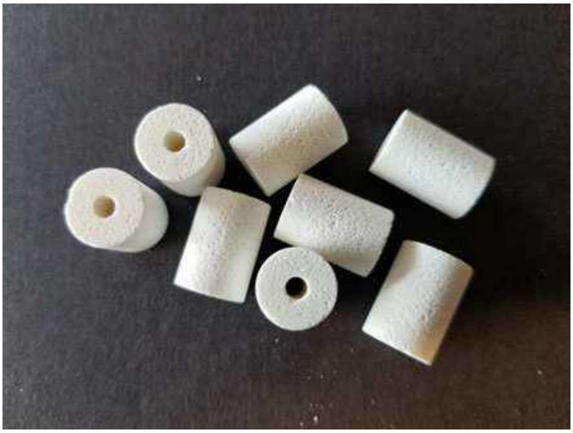


Fig. 7.5 White Hots® are a brand of muzzleloader pellets. © Crown copyright, Dstl

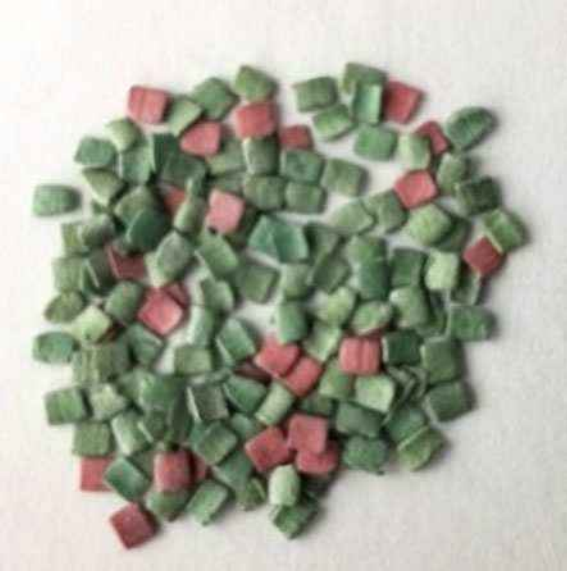


Fig. 7.6 Example of smokeless powder. Not all smokeless powders are black or gray, as illustrated by these pink and green lamels. © Crown copyright, Dstl

easily recognizable. The most common shapes are disk, tube (cylinder), rod, ball (sphere), flattened ball, lamel, and a catch-all irregular category, such as irregular flakes. Smokeless powders can also have perforations, examples of which are a hole in a disk or a hollow center through a cylindrical powder. The perforations increase the surface area and therefore the burning rate of the propellant. The perforation may not always be obvious to the naked eye as it can be obscured by an imperfection or coating during the manufacturing process. Many of the powders are black or gray, but some powders contain grains that are colored to aid identification. These colored grains are called markers or colored identifiers. The T/SWGFEX/NCFS Smokeless Powder Database is a useful online resource that contains images (micrographs), source information, physical and chemical properties and analysis parameters for over 800 different powders [10].

The principal component of smokeless powder is nitrocellulose, which is a highly flammable and energetic material. **Nitrocellulose**, or guncotton, is made by treating ordinary cotton with concentrated nitric and sulfuric acids. Smokeless powders are further classified as:

- single base: containing nitrocellulose (NC);
- double base: containing NC and nitroglycerin (NG); and
- triple base: containing NC, NG, and nitroguanidine (NQ).

Single and double base powders are the most common powders submitted to forensic laboratories; triple base powder grains are larger than single or double base powders and are found in higher caliber military-type munitions. Smokeless powders also generally contain a range of organic compounds including energetics, stabilizers, plasticizers, deterrents, flash reducers, and lubricants. Examples of these additives include 2,4-dinitrotoluene (2,4-DNT), trinitrotoluene (TNT), and diphenylamine (DPA).

Unlike commercial black powder, which has a single formulation, oxidizer/fuel mixtures can be highly variable. **Oxidizer/fuel** mixtures include commercial products, such as pyrotechnics and flash powders, and a wide range of improvised mixtures used in improvised explosive devices. Pyrotechnic stars for example come in a wide variety of compositions that, when ignited, produce different color effects and sparks. Typical oxidizer/fuel mixtures include nitrate, perchlorate, chlorate, and permanganate salts that can be mixed with a variety of fuels such as sugar, sulfur, and fine powdered metals including aluminum and magnesium. Examiners must exercise caution when handling these mixtures, particularly suspected flash powders, as they can be initiated by friction, static electricity, and impact. Some oxidizer/fuel mixtures can also function as high explosives. One example is flash powder.

Flash powders contain an oxidizer, commonly but not limited to potassium perchlorate or potassium chlorate, mixed with a metal fuel, such as magnesium, aluminum, or an alloy of the two, magnalium. Flash powders can be used as effect charges in commercial fireworks to produce a loud bang and/or flash for example, as the name suggests, or as a bursting charge.

7.2.2 High Explosives

As mentioned earlier, **high explosives** undergo **detonation** on initiation. Hot gases are produced, accompanied by a pressure wave, light, heat, and sound. There may also be a shattering effect from the pressure wave, known as **brisance**. Other high explosives produce a heaving effect and this property is used in industries, such as mining or tunneling, where the movement of large volumes of solid substances is required.

Unlike low explosives, which are mechanical mixtures of fuels and oxidizers, many high explosives are single molecules that can be thought of as chemically bound fuels and oxidizers. Structures of some of the more commonly seen explosives are shown below in Fig. 7.7. It should be noted that although many high explosives contain nitro-based groups, there are some high explosives that do not, such as peroxides.

High explosives can be further divided into primary, secondary, and tertiary blasting agent categories, depending on their susceptibility to initiation and their detonation velocity (Fig. 7.8) [11, 12].

Primary High Explosives

The more sensitive high explosives are referred to as **primary high explosives**. Historically, primary high explosives such as lead azide, lead styphnate, and mercury fulminate were not regularly submitted to forensic laboratories as they were not encountered very often by the law enforcement community when not part

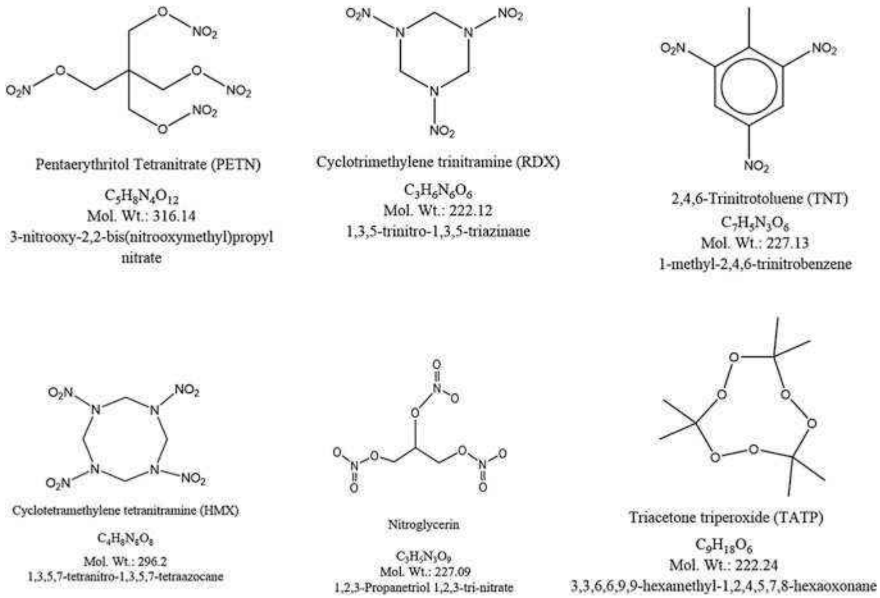

Pentaerythritol Tetranitrate (PETN)
$C_5H_8N_4O_{12}$
Mol. Wt.: 316.14
3-nitrooxy-2,2-bis(nitrooxymethyl)propyl nitrate
Cyclotrimethylene trinitramine (RDX)
$C_3H_6N_6O_6$
Mol. Wt.: 222.12
1,3,5-trinitro-1,3,5-triazinane
2,4,6-Trinitrotoluene (TNT)
$C_7H_5N_3O_6$
Mol. Wt.: 227.13
1-methyl-2,4,6-trinitrobenzene
Cyclotetramethylene tetranitramine (HMX)
$C_4H_8N_8O_8$
Mol. Wt.: 296.2
1,3,5,7-tetranitro-1,3,5,7-tetraazocane
Nitroglycerin
$C_3H_5N_3O_9$
Mol. Wt.: 227.09
1,2,3-Propanetriol 1,2,3-tri-nitrate
Triacetone triperoxide (TATP)
$C_9H_{18}O_6$
Mol. Wt.: 222.24
3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxonane

Fig. 7.7 Examples of molecular high explosives. © Crown copyright, Dstl

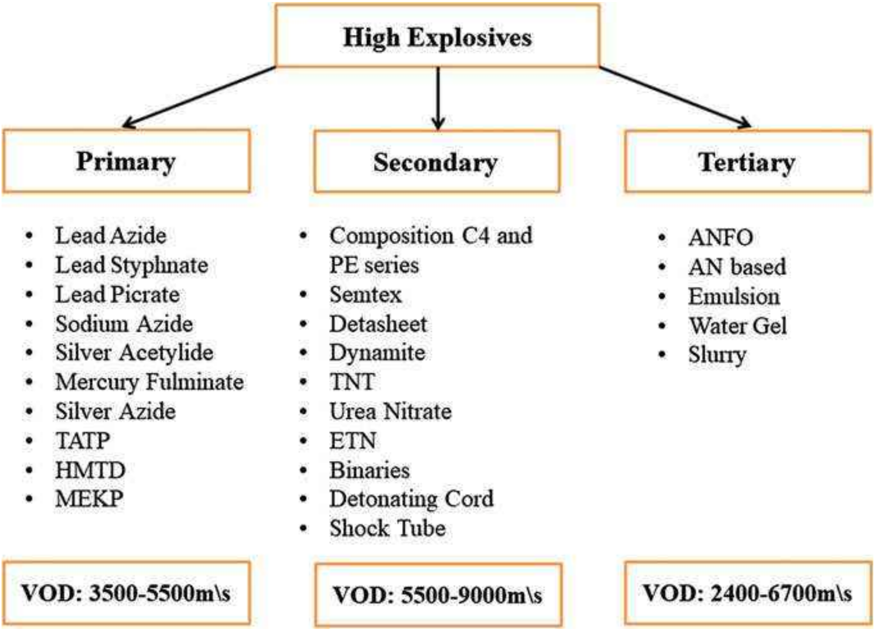


Fig. 7.8 Examples of high explosive products and the typical velocity of detonation (VOD) range for each category. It should be noted that some of these explosive products can fall into multiple categories depending on the precise formulation. © Crown copyright, Dstl

of a commercial detonator. Currently, a different range of primary high explosives, including organic peroxides, are encountered in the field and are routinely accepted and analyzed by laboratories.

Primary high explosives can detonate when exposed to a range of external stimuli such as heat, flame, friction, impact, or electrostatic discharge. Each primary explosive will have particular susceptibilities to different types of initiation; some are more susceptible to electrostatic discharge while others are very sensitive to heat, for example. Their ease of initiation means they are ideal for use in detonators, but also difficult to handle as more care is needed to protect them from such external stimuli and thus prevent accidental initiation.

A commercial **detonator** is a cylindrical metal shell containing both a primary and a relatively sensitive secondary high explosive, which is used to initiate larger quantities of other less sensitive secondary high explosives, known as the **main charge**. Within the detonator, the primary explosive initiates the secondary explosive, producing a shock wave that initiates the main charge. This is an example of an **explosive train,** an arrangement in which each explosive sets off another less sensitive, more powerful explosive. Detonators will be discussed more extensively in Chap. 9.

While the chemical analysis of the explosive content of commercial or military devices such as detonators is not typically required, samples of homemade primary explosives are sometimes submitted to the laboratory. These can include lead azide ($Pb(N_3)_2$), lead styphnate ($C_6HN_3O_8Pb$), triacetonetriperoxide (TATP), and hexamethylene triperoxide diamine (HMTD). Homemade explosives, particularly these primary explosives, can be extremely sensitive and are dangerous to handle for law enforcement and laboratory personnel. For example, TATP is prone to sublimation and can potentially recrystallize in the threads of the container that the TATP is being stored in, making handling of storage vessels potentially hazardous.

TATP and HMTD are peroxide-based primary high explosives that have no commercial or military uses because they are so easily initiated and, more importantly, unpredictable. TATP and HMTD can sometimes be differentiated by their appearance but not always, as illustrated in Fig. 7.9. Factors that affect appearance include the synthesis method and the precursors used, and whether a bulk amount or a small amount of crystals under a microscope is viewed. The appearance of TATP in particular can change dramatically with age due to sublimation.

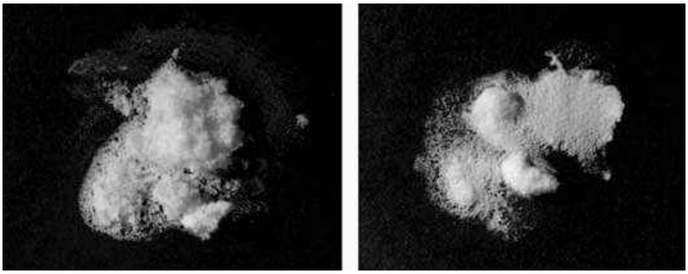


Fig. 7.9 TATP (left) and HMTD (right) are both white crystalline powders in their pure form. © Crown copyright, Dstl

Small amounts of TATP are used in improvised detonators and bulk amounts (kilograms) have been used increasingly in recent years in high-profile terrorist attacks in Paris (2015), Brussels (2016), Manchester Arena (2017), and the London Underground (2017).

Secondary High Explosives

Secondary high explosives are less sensitive than primary high explosives, usually requiring the shock wave from another explosion, such as that from a detonator, for initiation. Examples of secondary explosives submitted to laboratories can include military explosives containing RDX or TNT. Military explosives can have the same names as commercial explosives but different formulations.

Secondary high explosives can also be used for initiation of other explosives, such as in detonating cord and shock tube. **Detonating cord** is a thin flexible plastic tube usually containing PETN. **Shock tube** is a hollow plastic tube coated on the inside with a thin layer of HMX and aluminum. Both are used primarily to link several main charges (secondary or tertiary) together with almost simultaneous detonation. Explosive boosters are powerful secondary explosives that offer reliable initiation of non-detonator-sensitive blasting agents such as ANFO. When these boosters are cast into a cylindrical shell, which is generally made of cardboard or plastic, they are known as cast boosters. Boosters typically contain PETN or PETN/TNT mixtures. The detonator is generally placed inside the booster, which is placed inside the main charge.

Also within the secondary explosive category are commercial dynamites used for blasting. **Dynamite** comes in stick form, as shown in Fig. 7.10, and the explosive itself has a very distinctive appearance unlike any other explosive. Historically, dynamites contained nitroglycerin soaked into an adsorbent, which significantly

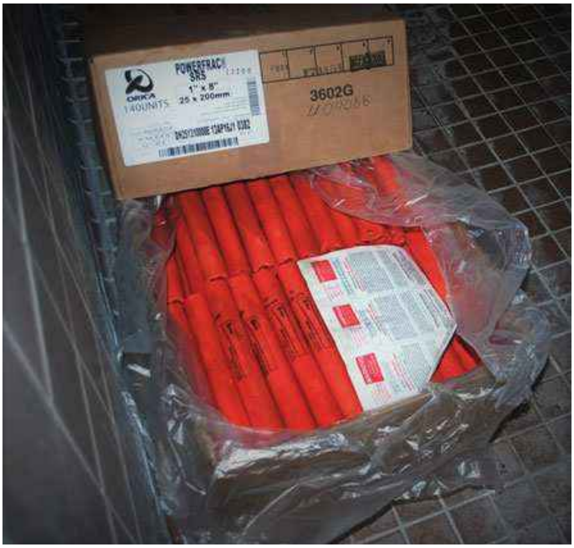


Fig. 7.10 Dynamite is a commercial high explosive. © Crown copyright, Dstl

decreases sensitivity. One potential issue for laboratories can be the receipt of old, or poorly stored dynamites, which have a tendency to leach liquid nitroglycerin, making them more susceptible to accidental initiation. There are a number of different formulations currently in use including straight, ammonia, gelatin, and semi-gelatin. Some ingredients that have been observed are the nitrate esters NG and ethylene glycol dinitrate (EGDN), ammonium nitrate, sodium nitrate, nitrocellulose, nitrostarch, wood pulp, sawdust, wax, and oil. It is also important to note that commercial dynamite and military dynamite have different formulations. The military version contains the organic explosives RDX and TNT and does not contain NG [13].

Plasticized explosives, colloquially known as plastic explosives, contain explosives, such as PETN or RDX, mixed with plasticizers, such as citroflex or dioctyl adipate, and other additives to make them malleable. They may also contain volatile chemicals as **chemical detection agents**, commonly referred to as 'taggants.' The most common examples of chemical detection agents are EGDN and 2, 3-dimethyl-2,3-dinitrobutane (DMDNB). Examples of plasticized explosives include Composition C4 and a range of Semtex products [13]. Detasheet is a plastic sheet explosive, a sub-group of plastic explosives that is named for the sheet form in which it is manufactured. Plastic sheet explosives can be shaped to meet particular needs and are often used to dispose of other explosives. The major components of plasticized explosives are shown in Table 7.1.

Polymer-bonded explosives (PBX) are sometimes confused with plasticized explosives but they are different. In PBXs, the explosive component, such as RDX or HMX, is bound together by a polymeric binder, commonly polyurethane, forming a rubbery composition which makes them easier to cast and less susceptible to shock and other stimuli. PBXs also contain plasticizers, bonding agents, wetting agents, cross-linkers, stabilizers, and catalysts. Aluminum is sometimes added as a fuel to increase blast effects.

Secondary explosives are generally highly regulated and carefully controlled. It is also possible, however, to form secondary explosives called **binary explosives** by combining non-explosive materials that are available commercially. Some 'exploding targets' used for target shooting contain pairs of packages of ammonium nitrate\aluminum powder or potassium perchlorate\aluminum powder that are mixed before use. Ammonium nitrate\nitromethane mixtures used in blasting as a main charge or as a booster are similarly prepared just before use.

Tertiary High Explosives (Blasting Agents)

A third category, known as **tertiary high explosives** or **blasting agents**, is used to describe high explosives which require a detonator and that may also require a

Table 7.1 Major components of common plasticized explosives (not including chemical detection agents)

Composition C4	Semtex	Detasheet
RDX Dioctyl adipate/sebacate Polyisobutylene Mineral oil	PETN (A) PETN and RDX (H) Plasticizer	PETN Nitrocellulose Binder

boosting charge (or booster) of a secondary explosive to produce their detonation. These are used for quarrying, mining, and tunneling and are further classed as slurries, gels, or emulsions.

Slurries consist of saturated aqueous solutions of oxidizers that contain dispersed sensitizing fuel and excess solid oxidants such as ammonium nitrate prills, which are small porous spheres. Various compositions exist, all of which are relatively insensitive to initiation. The mixtures can include TNT or non-explosive components that can act as a fuel, such as aluminum. Slurries are not seen often in the laboratory as they are usually mixed on-site as needed, providing less opportunity for theft.

Water gels, as their name implies, contain a gelatinizing agent (a thickener) to create the required consistency for a particular application, either for pouring or as a solid. Water gels can include ingredients such as monomethylamine nitrate (MMAN), ammonium nitrate, calcium nitrate, aluminum, ethylene glycol, and TNT. Polyvinyl alcohol (PVA), guar gum, dextran gums, and urea-formaldehyde resins can be used as the gelling agents.

Emulsion explosives, an example of which is shown in Fig. 7.11, are water-in-oil emulsions of oxidizer solution, usually ammonium nitrate, suspended as fine droplets that are surrounded by oils and waxes. Within the suspension are either ultra-fine air or gas bubbles or air encapsulated within glass beads (microballoons) which act as sensitizers. The percentage of ammonium nitrate varies between products depending on the required applications.

Commercially produced ammonium nitrate\fuel oil (**ANFO**) consists of prilled ammonium nitrate mixed with a small percentage of fuel oil and is also classed as a tertiary high explosive. Ammonium nitrate was used as part of the main charge in the Oklahoma City bombing in 1995. In that incident, TovexBlastrite Gel® was used to set off a configuration of barrels containing ammonium nitrate/nitromethane and ANFO mixtures. Homemade calcium ammonium nitrate/sugar mixtures, also classed as tertiary high explosives, were for many years the explosive of choice for the Provisional Irish Republican Army, causing much devastation and many millions of pounds worth of damage to cities across the UK.

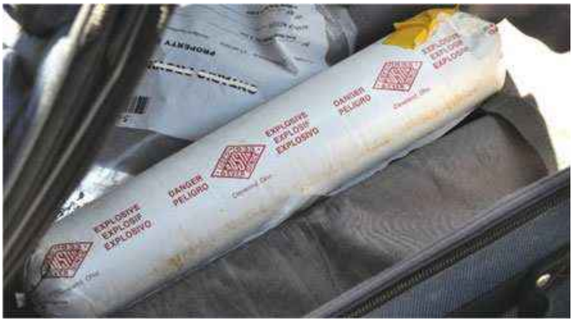


Fig. 7.11 An emulsion explosive in its original packaging. © Crown copyright, Dstl

Current Trends

Current trends in explosives submissions to major laboratories in the UK, Canada, USA, and the Netherlands are as follows:

- Low explosives which are still commonly submitted include black powder, smokeless powder, pyrotechnic mixtures, and homemade low explosives such as potassium permanganate/aluminum mixtures, and potassium nitrate/sugar mixtures.
- Commercial high explosives such as emulsions, dynamite, and plasticized explosives such as C4 and the PE-8 are not submitted as often as a decade ago, and Semtex is rarely seen.
- Peroxide-based explosives TATP and HMTD are increasingly common.

The most common devices are still improvised pipe bombs and package bombs though other containers such as buckets, pressure cookers, and paint cans are being submitted. Military ordnance, grenades, and detonators are still very commonly found in Europe and are seen in some North American laboratories.

7.3 Laboratory Analysis

There are few standardized methods available for the analysis of explosives. A variety of forensic organizations have begun to create standards for explosives analysis, beginning with smokeless powder [14, 15], but generally forensic chemists rely on published papers, textbooks [16–21], and standard operating procedures created in-house. A guide was written by the Technical and Scientific Working Group for Fire and Explosion Analysis (T/SWGFEX) [22]. The T/SWGFEX Guide, which was written by examiners, is still practical and useful, even though some of the instrumentation listed is outdated due to advances in instrument detectors.

The analysis of intact explosives is qualitative and spans the range of forensic expertise from the knowledge of appearance to the application of complex instrumentation. Due to the broad range of types of explosives, it is not practical to deliver a step-by-step guide for the analysis of explosives. Instead, a more practical approach that emphasizes a general analytical scheme will be presented.

7.3.1 Safety and Packaging

Acceptance of explosive samples for laboratory analysis begins with the initial assessment of the packaging of the sample. Safety is of primary importance and while some general guidelines are given here, forensic examiners must be knowledgeable in the properties and hazards of explosives. The packaging and contents

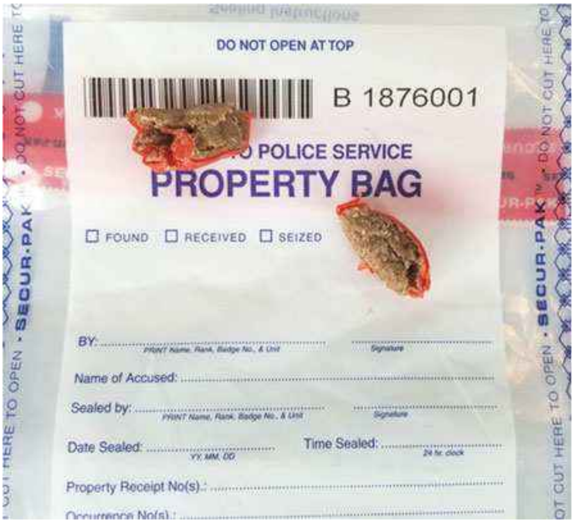


Fig. 7.12 A sample of dynamite packaged in a polyethylene bag for submission to the laboratory. © Crown copyright, Dstl

(if visible through the packaging, as in Fig. 7.12) should be assessed for potential safety and analytical concerns, and a determination made if an item is too dangerous to handle in its current condition, such as dynamite leaching nitroglycerin or intact rusted hand grenades. Although commercial and military explosives are relatively stable and safe to handle, the examiner must understand that they do not know how the item has been stored or treated during its lifetime and cannot be certain that it has not been modified, until it is tested.

In general, many explosives can be safely packaged in vials or anti-static (usually indicated by being pink) plastic bags. Care should be taken when opening screw-top vessels, as dry, friction-sensitive powders can potentially be initiated by the act of unscrewing the lid. As mentioned previously, TATP sublimes and can potentially recrystallize in the threads of a screw-top vessel. Any container suspected to contain TATP should be examined carefully for possible recrystallization prior to opening. Ideally, samples of suspected TATP, HMTD, or other peroxide-based explosives will be small (less than one gram) and placed in an appropriate solvent/solution prior to submission, such as isopropanol, ethanol, and a 1:1 ethanol/water mixture.

When examining the packaging, consideration also needs to be given to the types of analyses that will be able to be performed. Some explosive compounds, such as EGDN, TATP, and chemical detection agents, are volatile, giving off vapors that can be captured and analyzed in the laboratory. Explosives that require vapor analysis should be packaged in vapor-tight containers, such as those discussed in Chap. 2 (see Fig. 7.13).

Ad hoc packaging is sometimes required for safety reasons, and the rationale for it must be clearly enunciated and documented to avoid confusion later. Samples of homemade mixtures, such as the concentrated hydrogen peroxide/chapatti flour

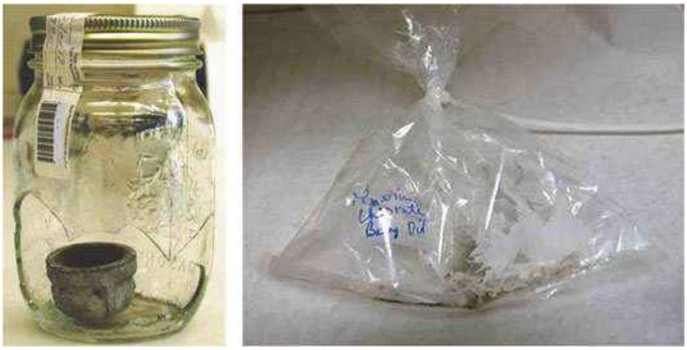


Fig. 7.13 The figure on the left shows a submission that was packaged in a glass jar, which was not ideal. The figure on the right shows a speciality nylon bag that can be used to retain explosives vapors. © Crown copyright, Dstl

mixtures recovered in the devices used in a failed London attack (2005), are a case in point. In this incident, the hydrogen peroxide was reacting with the flour, producing a hazardous gas. An intentional hole was created in the packaging to vent the gases produced, thus avoiding rupture during transit and storage.

7.3.2 Sample Appearance and Presumptive Tests

The starting point for the examination of any material suspected to be an explosive is the observation of physical characteristics including shape (morphology) and color. Based on the appearance of the material and potentially background information from an investigator, the examiner typically can preliminarily determine the general type of explosive (i.e., oxidizer/fuel mixture, commercial black powder, plasticized explosive) as a guide for the analysis. Most laboratories maintain reference collections of explosives and photographs for comparison and training purposes. There are also textbooks and online resources [10, 23] that provide photographs and descriptions of commercial, military, and improvised explosives.

Samples should also be viewed under a stereo light microscope before a specific analytical scheme is decided upon. Examination under the microscope may reveal the presence of a mixture of explosives, such as a variety of morphologies of smokeless powder or a mixture of black powder and black powder substitutes. Each type of visually different explosive should be separated out for identification. A material packaged in a sausage-like casing could be an emulsion or a water gel explosive, both of which are used extensively in the mining industry but have different ingredients and appearances under the microscope. Water gels/slurries, as the name suggests, have a ‘jelly-like’ appearance, whereas emulsions have a consistency more like cream cheese.

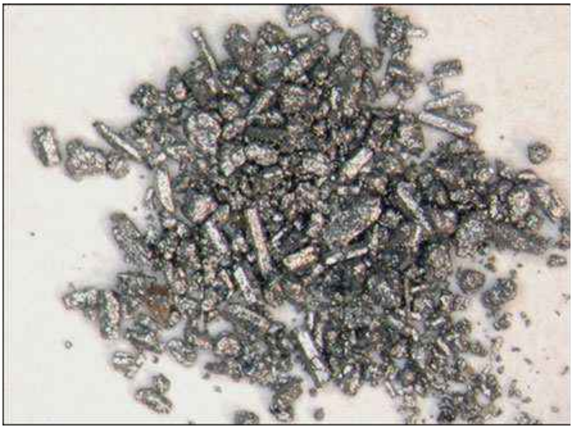


Fig. 7.14 An actual case submission of TATP coated with aluminum powder. © Crown copyright, Dstl

Unknown powders can be difficult to categorize on initial visual inspection. As an example, somewhat gray powder submitted to a laboratory was initially assessed as having the appearance of a pyrotechnic mixture like flash powder. A few crystals were placed under a stereo light microscope for examination. On splitting some crystals, the examiner noted a white material inside, shown in Fig. 7.14, which was disappearing. This was suggestive of sublimation, typical of TATP as previously mentioned. The white crystals were ultimately identified as TATP, and the gray coating was identified as aluminum. This case example highlights why suspected explosives materials should always be viewed under, at minimum, a stereo light microscope to confirm the initial assessment.

Once a preliminary assessment has been made, the sample can then be further characterized by presumptive tests to ensure that the most appropriate course of analysis is chosen. These presumptive tests can also be performed after instrumental testing for additional confirmation. The most useful presumptive tests for the forensic examiner are **burn test** (ignition\thermal susceptibility test, or IST) and chemical **spot tests** [24–26]. Both types of presumptive testing are destructive, so should only be used if there is sufficient sample available to perform more definitive analyses. The results of all presumptive tests should be recorded in detail and can be augmented by photographs.

Burn tests are performed by exposing a small sample of the suspected explosive to open flame. Examiners should be familiar, through practice, with the burn characteristics of all classes of explosives. For example, TATP produces a fireball with no smoke, as shown in Fig. 7.15. Commercial black powders will deflagrate with significant smoke generation. A homemade powder, on the other hand, may not be well mixed and therefore may burn less effectively, providing an indication for the forensic examiner that the powder may be improvised.

A burn test should only be performed on a small amount of material as some of the reactions can be violent, producing flame, noise, and copious amounts of smoke. Materials such as pyrotechnic stars, fuses, and pelletized black powder

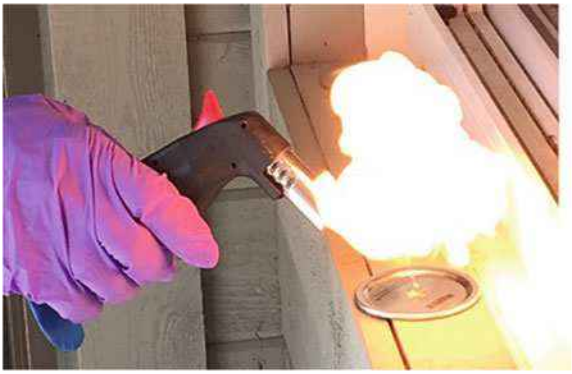


Fig. 7.15 Characteristic fireball produced when TATP powder is burned. © Crown copyright, Dstl

substitutes may also move rapidly across the laboratory when ignited. Therefore, a safe area such as a fume hood should be used, and no combustible or flammable materials nearby. Descriptive language should be used to document the reaction. For example, ‘the powder ignited immediately, burned rapidly, produced a lot of white smoke and left a black residue,’ and ‘an energetic reaction was observed that produced a yellow fireball and no residue remained.’

Chemical spot tests use known chemical reactions with predictable color or fluorescent results to test for particular analytes. There is a wide range of chemical spot tests available to indicate the presence of ions including nitrate, chlorate, sulfate, chloride, and ammonium that are associated with explosive materials. Positive and negative controls should always be performed contemporaneously to ensure that the test reagents are working as expected at the time that the test is conducted. The positive control should always be performed after the test on the samples to minimize the risk of cross-contamination. These tests are quite specific but must not be used as the sole method to identify compounds.

There are techniques that do not fit into the ‘chemical spot test’ or ‘instrumentation’ categories. The most obvious examples are polarized light microscopy (PLM) and thin-layer chromatography (TLC). These are other excellent tools for the analysis and identification of some explosives.

Polarized light microscopy (PLM) is a mature, non-destructive analytical technique that is used in some laboratories to identify explosives by their physical and optical properties. In PLM, light passes through a polarizer prior to interacting with the sample and through an analyzer before reaching the eyepieces or camera. A skilled examiner can use a combination of morphology, crystal structure, birefringence and refractive index to identify explosives and explosive-related particles or to isolate particles for further analysis.

Thin-layer chromatography (TLC) used in the laboratory is a simplified version of the chromatographic techniques discussed in Chap. 1 and can be used for qualitative screening of nitrates, nitramines, nitrate esters, and organic peroxides. TLC is a useful, if basic, technique which can be used to support other more advanced laboratory techniques. In many laboratories, modern chromatographic-mass spectrometry instrumentation has displaced the use of TLC, as it can provide mass spectral information.

TLC uses plates coated with a fine uniform layer of an adsorbent such as silica or cellulose. Solid samples are dissolved and spotted onto a plate alongside the appropriate laboratory controls and explosives reference solutions. Following elution, the retention factor (Rf) of any developed spots is calculated. The presence of an explosive can be supported by the comparison of the Rf, UV activity, and the color of the developed spots with the explosive standards, as shown in Fig. 7.16.

Other tests, such as solubility or pH, may also be useful for screening suspected explosives. For example, during the examination of gray/black cylinders submitted to the laboratory for explosive analysis, the cylinders on first glance appeared to be smokeless powder based on their shape and color. The material did not burn energetically, and a few grains placed in acetone did not break down forming a gel, as would be expected from a smokeless powder. Analysis revealed the presence of graphite but no other components of smokeless powder, confirming that 'pencil lead' had been submitted.

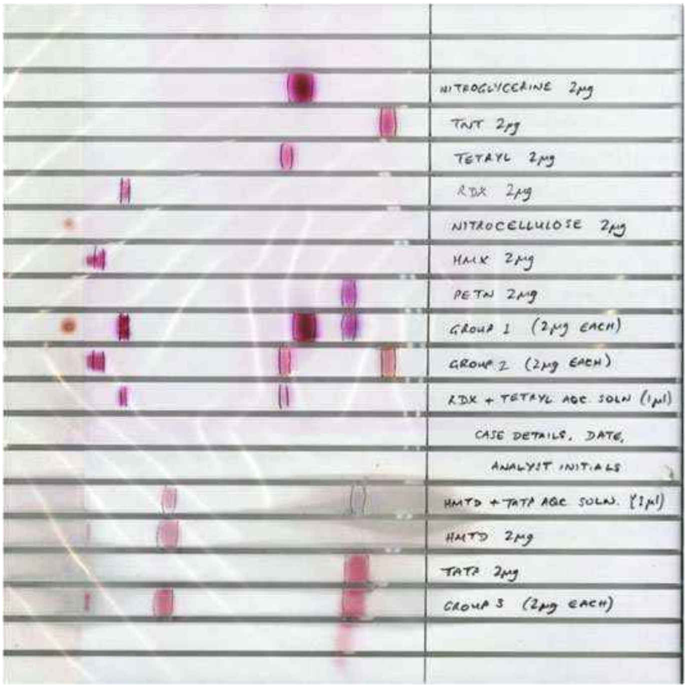


Fig. 7.16 Eluted and visualized TLC plate showing the separation of a range of explosive compounds. © Crown copyright, Dstl

7.3.3 Instrumental Analysis

There is a range of well-established advanced analytical techniques used by forensic laboratories for the analysis of explosives; the theory behind each of these instrumental techniques is discussed in Chap. 1. The question of what constitutes the **identification** of a particular component is an important question, and the answer is highly dependent on the laboratory and what type of explosive it is. An unambiguous identification cannot always be made from the data obtained from a single analytical technique. Elemental techniques, which are generally not good for identification of anything but pure elemental components like sulfur, provide information that informs the techniques that *can* provide molecular identification.

Most laboratories have standard operating procedures that require the use of **orthogonal techniques** to make an identification and minimum criteria for each particular technique. Some analytical instruments combining two separate analytical techniques, such as LC-MS, can be considered to suffice without further supporting techniques. For example, for a particular substance to be identified using liquid chromatography–mass spectrometry (LC-MS), the substance to be analyzed has to be soluble in the solvent used, to be compatible with and separated by the LC column, to elute within the retention time window of the explosive in question, to survive the ionization process and have the same mass to charge ratio as the substance in question. Other techniques that are much less selective, such as TLC, will require at least a secondary confirmatory technique.

The choice of analytical techniques used largely depends on the types of compounds expected to be present in the sample. The majority of low explosives, with the exception of smokeless powder, contain mainly inorganic compounds. The oxidizers are generally nitrate, chlorate, or perchlorate salts that are easily identified by combinations of techniques such as Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy–energy-dispersive spectroscopy (SEM-EDS). Other techniques, either singly or in combination, may also be used for identification. The fuels and other additives in both low and high explosives are more variable and can require a broader range of analyses, including gas chromatography–mass spectrometry (GC-MS), LC-MS, ion chromatography–mass spectrometry (IC-MS), FTIR, and XRD. This variability in the instruments needed highlights the necessity of visual screening and familiarity with the common low explosives.

7.4 Identification of Explosives

The identification of an explosive material requires visual examination and identification of the major individual components of the explosive material. For less complex explosives, this is relatively simple. For example, TATP is a single-component explosive that can simply be recognized by the white powdery appearance and burn test, and identified by FTIR or XRD analysis. As the explosives get more complex, more instrumentation and information are required for identification.

7.4.1 Black Powder and Black Powder Substitutes

The oxidizer in black powder is potassium nitrate, which is easily identified by a combination of SEM-EDS and FTIR or XRD. Black powder also contains elemental sulfur, which can be identified by a broad variety of techniques including XRD (Fig. 7.17), Raman (Fig. 7.18), and PLM. Commercial black powder could be identified by the following combination of analyses:

- Appearance: black angular particles;
- Burn test: white smoke, rapid flame;
- SEM-EDS: C, N, O, S;
- XRD: potassium nitrate, sulfur;
- Raman: sulfur;
- If necessary, a spot test can confirm sulfur if XRD data is not available or sufficient.

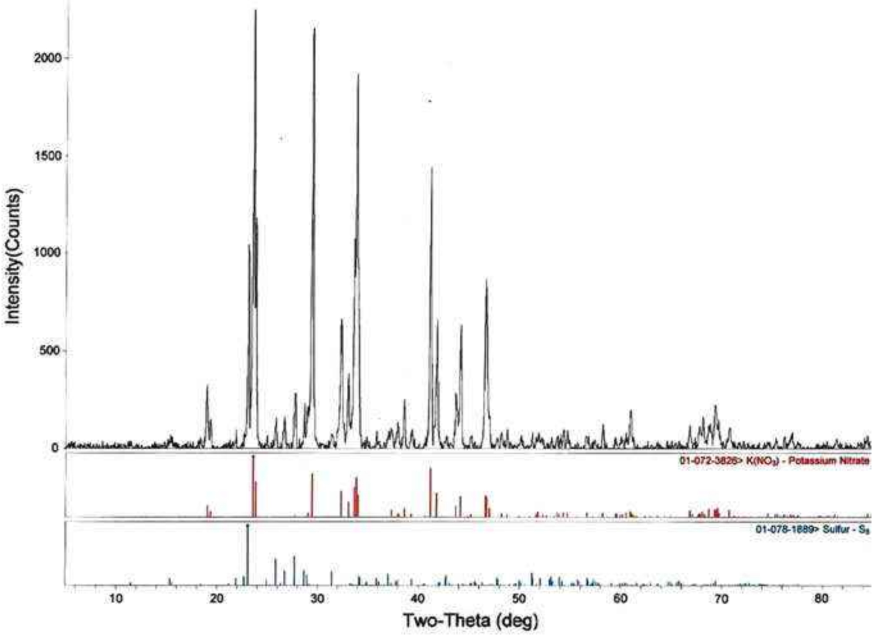


Fig. 7.17 X-ray diffraction pattern of a black powder propellant (top). The d-spacings for potassium nitrate (middle) and sulfur (bottom) are shown. © Crown copyright, Dstl

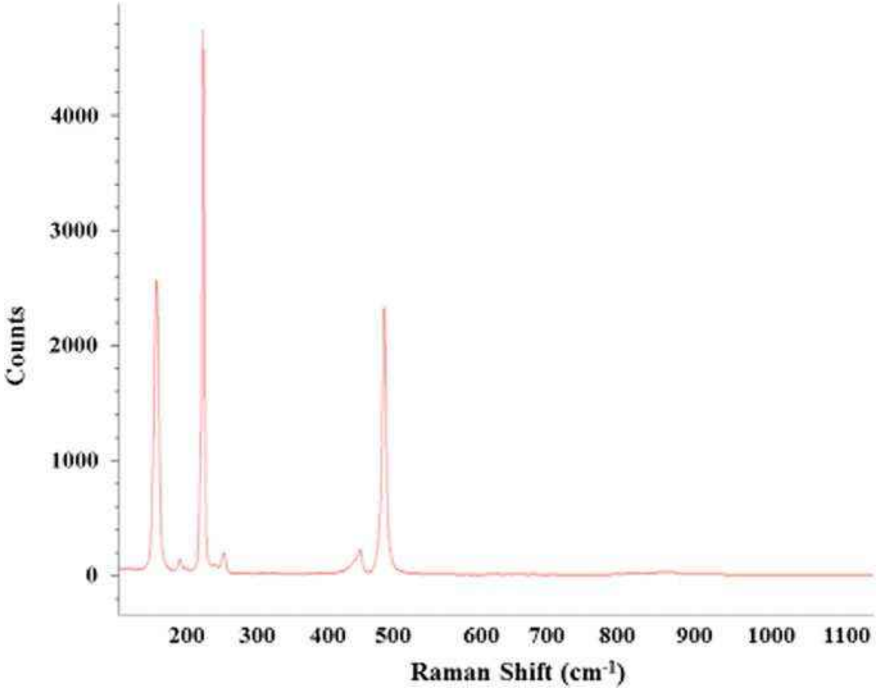


Fig. 7.18 Raman spectrum of sulfur. © Crown copyright, Dstl

Black powder also contains charcoal, which is generally too finely ground in commercial black powder to be identified. In coarser homemade black powder, charcoal can be identified using SEM-EDS by looking for a 'honeycomb' structure with the strong presence of carbon.

Black powder substitutes generally include fuels such as sodium benzoate, DCDA, 3-nitrobenzoate, and ascorbic acid. DCDA is not effectively identified within the complex mixture that is Pyrodex® or Triple Seven® without some form of separation technique; as such, LC-MS would be necessary to identify DCDA. In contrast, ascorbic acid can be easily identified by all of the techniques listed above.

Black powder substitutes can also be relatively simple to characterize. For example, Pyrodex® can be characterized as follows:

- Appearance: gray agglomerated particles with white inclusions;
- Burn Test: white smoke, rapid flame;
- SEM-EDS: C, N, O, S, Cl, K;
- XRD: potassium nitrate, potassium perchlorate, sulfur;
- If necessary, the DCDA and sodium benzoate can be characterized using an LC technique.

It is impractical to discuss every single explosive that can be identified, but some of the more complex explosive mixtures will be discussed to demonstrate a general approach to the identification of explosives.

7.4.2 Smokeless Powder

The initial step in identifying smokeless powder is to conduct visual and microscopic examinations, during which the appearance of the grains is documented. The appearance includes morphology, color, shape, and texture as well as the presence of perforations and any colored identifiers. The holes that run along the length of tubular propellant can sometimes be obscured by graphite, requiring close inspection. The outer graphite coating may come off over time through contact, which changes the color from black\gray to the interior color of the grain, which is generally green or yellow. Other characteristics to note are the diameter, length, and thickness (as appropriate) of grains, which can be measured using a ruler or micrometer, bearing in mind that there will be some variability due to the manufacturing process. Measurement is not required for identification but is necessary when comparing powders, which will be discussed further later. A burn test can also be performed if there is sufficient sample available. Smokeless powders will ignite easily and burn energetically with negligible smoke generation.

The instrumental analysis typically begins with the identification of nitrocellulose using FTIR. The presence of nitrocellulose alone combined with the morphology is enough to identify a powder as smokeless powder [14]. Nitroglycerin has a similar infrared spectrum to nitrocellulose (Fig. 7.19) and can interfere with an identification if present in the powder. It is possible to interpret the mixed spectrum; however, the two components may also be isolated by liquid–liquid extraction prior to analysis as nitrocellulose is soluble in acetone but not dichloromethane, and nitroglycerin is soluble in both [14]. As such, a dichloromethane rinse of a dissolved and re-solidified smokeless powder particle can effectively separate these two components.

The nitroglycerin and other additives can also be identified using a combination of techniques including GC, LC, capillary electrophoresis (CE), and MS. It should be noted that smokeless powders from different sources that have been mixed together for a period of time can result in migration of nitroglycerin and additive components from one powder to another. Caution should thus be exercised when classifying mixtures of powders as double base or comparing mixtures of powders.

The myriad of different morphologies and additives provide many points of comparison that can be used to link powders; for example, grains found in a device can be compared to a can of powder found at a suspect’s residence. The varied additives in smokeless powders, including stabilizers, plasticizers, and flash suppressants, can be used to identify or discriminate between powders [27].

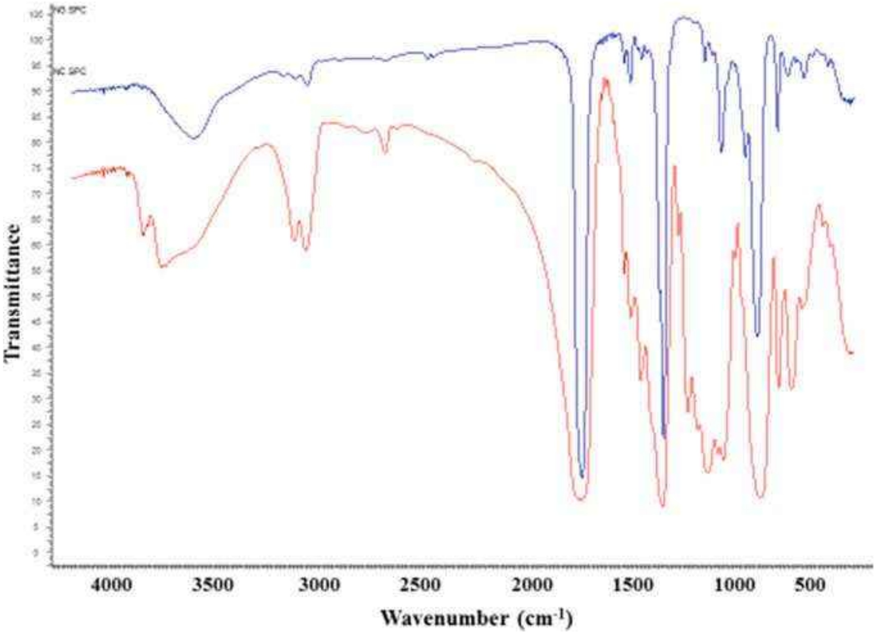


Fig. 7.19 FTIR spectra of nitroglycerin (blue) and nitrocellulose (red). © Crown copyright, Dstl

Figure 7.20 shows a smokeless powder comparison that was requested in an actual case. Chemical analysis is still necessary for the identification of the sample as smokeless powder, but the diameters of the disks are clearly visually different.

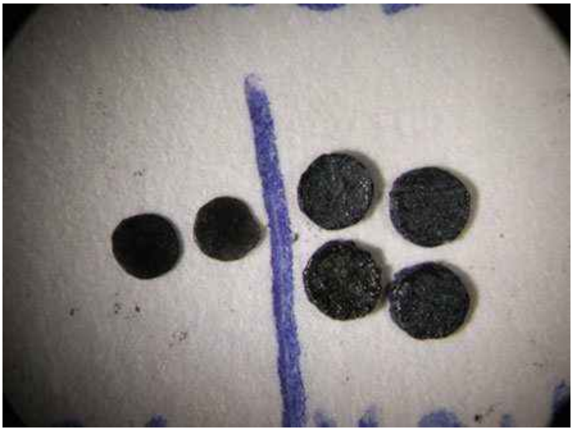


Fig. 7.20 A comparison of smokeless powder disks from a case. The difference in the diameter of these disks is readily apparent even to the untrained eye. © Crown copyright, Dstl

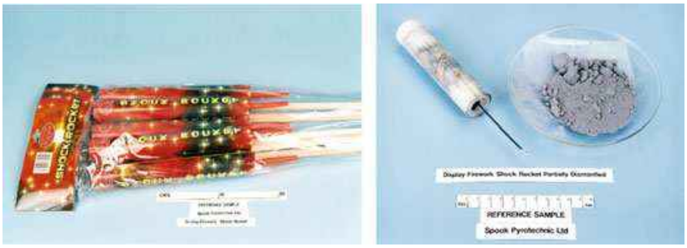


Fig. 7.21 A package of 'Shock Rocket' fireworks (left) and an individual firework from the package dismantled for analysis (right). © Crown copyright, Dstl

7.4.3 Oxidizer/Fuel Mixtures

Oxidizer/fuel mixtures include pyrotechnics, which are usually recognizable as commercial products (Fig. 7.21) and are uniform in shape and particle size, commercial flash powders, and homemade mixtures that may or may not have a homogenous factory-made appearance. An early indication of their energy is important to establish through a burn test, if there is sufficient material. Oxidizer/fuel mixtures will burn rapidly and may emit light, sound, sparks, and smoke. Improvised mixtures will burn fitfully if not well mixed. Spot tests are useful indicators of the presence of both oxidizers and fuels.

Oxidizer/fuel mixtures, which by definition are mixtures of different chemicals, are more difficult to analyze and identify with the increased complexity of the mixture. For example, a simple mixture such as flash powder that contains one oxidizer, potassium perchlorate, and a metal fuel, aluminum is straightforward to analyze. The aluminum or other metals can be identified using XRD with X-ray fluorescence (XRF) or SEM-EDS. As previously discussed, the potassium perchlorate can easily be identified by FTIR or XRD with an elemental technique. On the other hand, more complex mixtures can be more challenging and it may be necessary to use water extraction to separate the various components. For example, potassium nitrate can be isolated if necessary by a simple water extraction and recrystallization by evaporation. Alternatively, a water extraction can provide a simple means to separate out insoluble metal fuels from a mixture for better characterization. Examples of particularly complex mixtures are road flares or homemade hypergolic mixtures; their ingredients and analysis are covered in detail in Chap. 10.

7.4.4 High Explosives

Many high explosives will require GC-MS or LC-MS for identification. Relatively simple explosives, such as the PETN filler in detonating cord, can be identified very easily by XRD or FTIR with minimal preparation. Other high explosives may require extensive preparation before analysis, particularly plasticized explosives. Sequential solvent extraction may be necessary to separate the components sufficiently for identification.

Primary high explosives will react very energetically when exposed to heat during the burn test alerting the examiner to the probability that the powder is a primary high explosive that must be handled with extreme caution. The common techniques used in the analysis of inorganic explosives discussed previously (such as FTIR, XRD, and SEM-EDS) are also the analytical techniques of choice for the inorganic primaries. Pure organic peroxides (TATP, HMTD, and methyl ethyl ketone peroxide (MEKP) are routinely identified using FTIR with little or no sample preparation. Raman can also be used with a few provisos; more sample is needed than for FTIR unless a microscope attachment is available, and there is a possibility than the Raman laser may initiate the sample by heating, particularly for instruments that utilize a ‘spot’ laser. GC-MS and LC-MS are also techniques for unequivocal identification of these compounds.

As mentioned in Sect. 7.3.2, water gels/slurries have a gelatinous appearance, while emulsions have a thicker consistency. They can contain suspended ammonium nitrate (and/or sodium nitrate) in powder or prill form and various fuels (e.g., metal flakes) and sensitizers (e.g., microballoons). The prills are visible under a stereo light microscope and can generally be identified using XRD and FTIR with elemental analysis. The microballoons (shown in Fig. 7.22) and metal flakes may require viewing under a high power microscope and may be analyzed using SEM, with additional XRD analysis for the metal flakes as necessary. MMAN is another sensitizer that may be present and can be analyzed by LC-MS, XRD, or FTIR, though the hygroscopic nature of MMAN may require additional sample

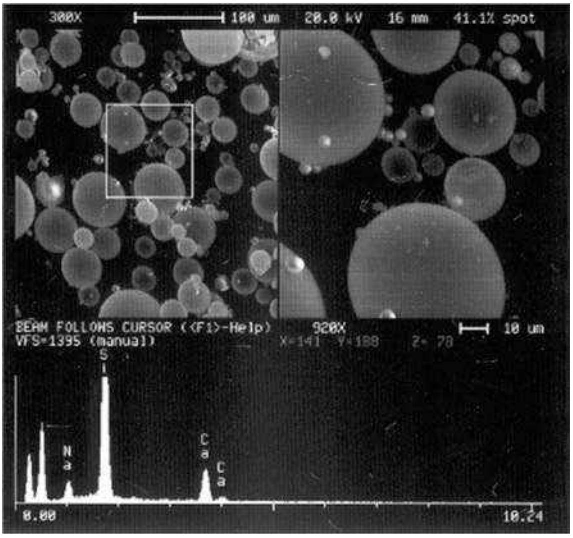


Fig. 7.22 SEM-EDS analysis of an emulsion explosive sample. The presence of Na, Si, and Ca elements showed the presence of glass microballoons. © Crown copyright, Dstl

preparation. A series of solvent extractions can be used to differentiate between emulsions and water gels and isolate the above components of interest prior to analysis. For example, the components of emulsions can be separated by extraction with an organic solvent, such as hexane, which will retain lubricating oils or waxes, followed by water, which will remove any inorganic salts like ammonium nitrate. Microballoons or metallic flakes will also typically float on top of these extracts and can be filtered out or skimmed off for easy analysis.

Dynamite is another secondary explosive with relatively complex formulations. The analysis of dynamite is preceded by solvent extractions and filtering to isolate the main ingredients for instrumental analysis and identification. NG and EGDN can be removed by washing the dynamite sample thoroughly with dichloromethane or doing a headspace extraction; this fraction is typically analyzed by GC-MS or LC-MS (Fig. 7.23). The remaining sample can be washed with acetone to dissolve NC or nitrostarch, if present; the acetone may need to evaporate or water may need to be slowly added to the liquid in order to get NC into a form that can be identified by FTIR.

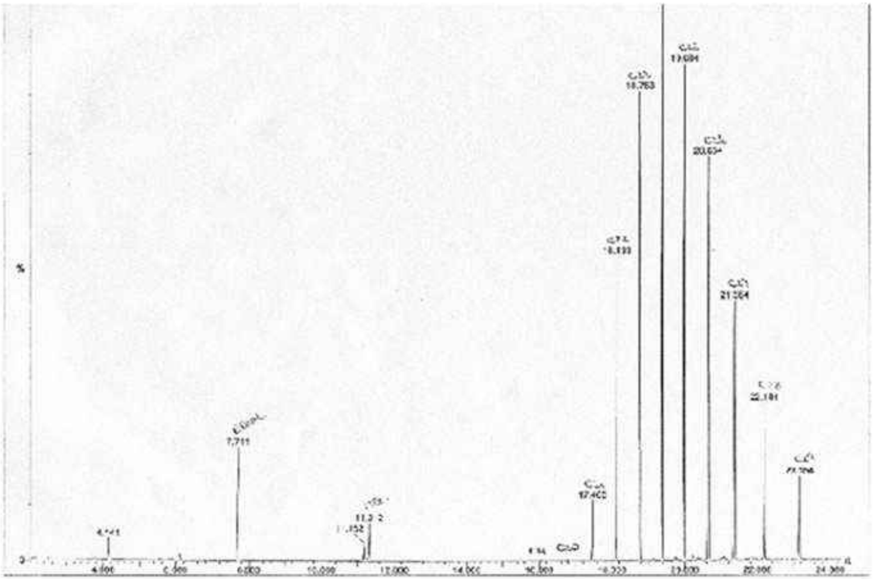


Fig. 7.23 Pieces of torn orange wrapper suspected to originate from dynamite were submitted to the laboratory for analysis. EGDN, NG, and a series of normal alkanes (C20–C29), which act as fuel, were extracted using hexane and identified by GC-MS. © Crown copyright, Dstl

A water wash of the solid sample will dissolve the ammonium nitrate and\or the sodium nitrate, if present. The solid material that remains, such as fillers and microballoons, can then be examined separately.

As previously discussed, ANFO is a mixture of a solid oxidizer, ammonium nitrate, and a fuel oil, such as diesel fuel. The presence of prills will be an obvious physical characteristic, and the ammonium nitrate can be identified using techniques such as FTIR and XRD. The fuel oil can be extracted using headspace techniques or solvent extraction. Nitromethane (NM) is an energetic liquid (classified in some jurisdictions as an explosive) that can be mixed with a range of oxidizers (including ammonium nitrate), sensitizers, and fuels. Nitromethane will ignite easily and sustain a flame when burn tested. The liquid can be identified using techniques such as GC-MS, FTIR, and Raman. The analysis of ANFO and AN\NM, which potentially involves the analysis of ignitable liquids (fuel oil and NM) with an explosive component (ammonium nitrate), will be discussed further in Chap. 10.

Examiners will follow a path similar to the one shown in Fig. 7.24, based on available techniques, experience, and laboratory requirements. The following case submission illustrates how this analysis scheme might be used.

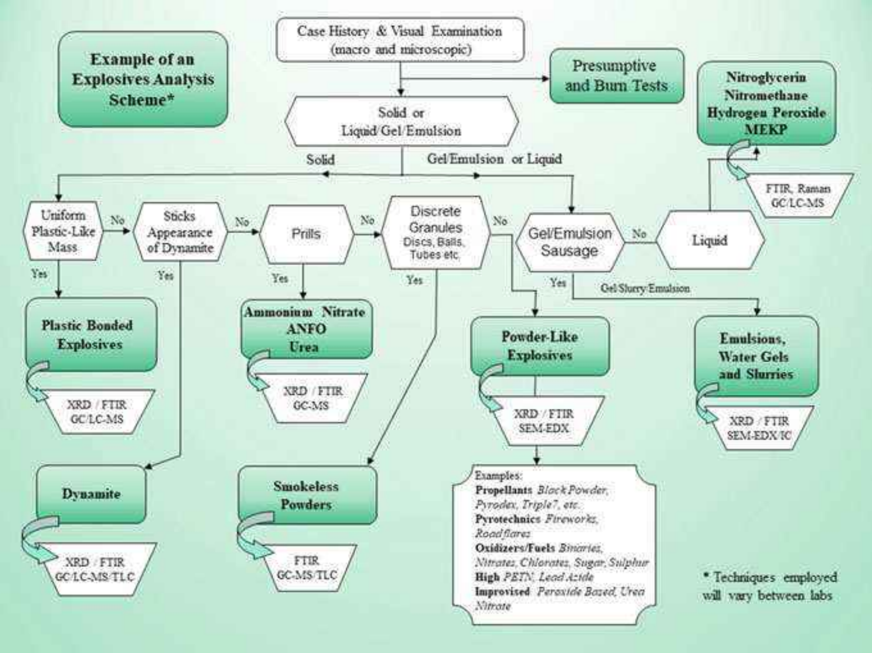

Example of an Explosives Analysis Scheme*
Case History & Visual Examination (macro and microscopic)
Presumptive and Burn Tests
Nitroglycerin Nitromethane Hydrogen Peroxide MEKP
Solid or Liquid/Gel/Emulsion
Solid
Gel/Emulsion or Liquid
FTIR, Raman GC/LC-MS
Uniform Plastic-Like Mass
No
Sticks Appearance of Dynamite
No
Prills
No
Discrete Granules Discs, Balls, Tubes etc.
No
Gel/Emulsion Sausage
No
Liquid
Yes
Yes
Yes
Yes
Yes
Gel/Slurry/Emulsion
Plastic Bonded Explosives
Ammonium Nitrate ANFO Urea
Powder-Like Explosives
Emulsions, Water Gels and Slurries
XRD / FTIR GC/LC-MS
XRD / FTIR GC-MS
XRD / FTIR SEM-EDX
XRD / FTIR SEM-EDX/IC
Dynamite
Smokeless Powders
XRD / FTIR GC/LC-MS/TLC
FTIR GC-MS/TLC
Examples:
Propellants Black Powder, Pyrodex, Triple7, etc.
Pyrotechnics Fireworks, Roadflares
Oxidizers/Fuels Binaries, Nitrates, Chlorates, Sugar, Sulphur
High PETN, Lead Azide
Improvised Peroxide Based, Urea Nitrate
* Techniques employed will vary between labs

Fig. 7.24 Analysis of intact explosives can be complicated, as illustrated in this example of an analytical flowchart. © Crown copyright, Dstl

7.4.5 Case Study

An IED was thrown into a public house (pub) on a busy Friday night in the UK, but did not function. Police were called and the IED was rendered safe by explosive ordnance disposal (EOD—bomb disposal) officers. The device components were submitted to the laboratory for analysis (Fig. 7.25). A glass coffee jar held a metallic gray powder and a large number of nails, tacks, and screws. The top of the jar had a white plastic tube protruding, secured to the jar with blue tape. The investigating team asked if the device was viable, what was the explosive and why did it fail to go off?

During the burn test, the metallic powder ignited immediately and burned very quickly with a bright white flash with some smoke generated. This burn test indicated that the powder was a very quick-burning low explosive, most likely a flash powder. It was clear that the powder did not fit the descriptions or burn characteristics of black powder, black powder substitutes, or high explosives. Therefore, the powder was initially analyzed by SEM-EDS and FTIR.

SEM-EDS showed the presence of predominantly aluminum, potassium, and chlorine, supporting the results of the burn test. Potassium perchlorate could not be identified by FTIR due to the presence of the metal fuel, which interfered with the spectrum. Therefore, the sample was further analyzed by IC to confirm the presence of perchlorate and potassium. The appearance, burn characteristics, and analytical results combined revealed the gray powder to be a flash powder.

The white plastic tube taped into the mouth of the jar contained a length of Visco fuse protruding from one end and a beige clay plug in the other end. A fine black-colored powder was visible at the end into which the fuse protruded. Gentle scraping of this compacted powder gave enough sample to carry out a burn test. The powder ignited immediately and burned very quickly with a bright yellow flame. The burn was not as fast as that of the flash powder sample and was more similar to black powder.

Enough sample was obtained for a full analysis, including:

- FTIR: Potassium nitrate;
- SEM-EDS: potassium, sulfur, and carbon;
- IC: nitrate, potassium, and a lower level of sulfate.

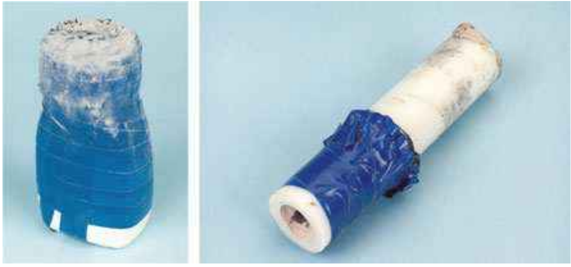


Fig. 7.25 Coffee jar (left) containing a metallic powder and a plastic tube originally attached to the jar were submitted to the laboratory for analysis. © Crown copyright, Dstl

Collectively, these results supported the presence of black powder which contains potassium nitrate, sulfur, and charcoal. The device may have failed because, though burning was apparent at the end of the fuse, parts were bent and weakened, thus probably leading to the failure of the fuse to burn to its end.

7.5 Reporting Explosives

The explosives examiner's role is to identify the presence or absence of an explosive in the submitted material. After completing a thorough and appropriate analysis, the forensic examiner will summarize their findings in a clear and concise written report. The range of services offered varies between laboratories and influences the contents of the report. The format and language used will also differ because of laboratory policies and location.

Some laboratories will choose to report the individual components identified in a 'results' section, with a separate 'conclusion' section for the identification of intact explosives, based on those individual components. For example:

Results: A sample of Item 1 contained the major components: nitrocellulose, 2,4-dinitrotoluene, and diphenylamine.
Conclusion: Item 1 is classified as a single-base smokeless powder.

Other laboratories may combine these two sections or will simply report the identification of the explosive. There may also be a discussion section to mention factors that affect the conclusions, such as the alternative uses for an identified component. For example, a sample of Item 1 contained nitroglycerin, an explosive found in double base smokeless powders and commercial dynamites. When pure, it is a colorless oily liquid. Nitroglycerin can also be found in some heart medications.

Depending on laboratory protocols and the case needs, other information may also be included with the identification of the explosive. Examples of these include:

- Common uses\properties of the identified explosive;
- Efficacy of the explosive;
- Possible methods of initiation;
- Potential effects of the explosion of explosive, given quantity and reported method of containment;
- Notation of possible 'homemade' mixture if it did not appear to be well mixed or did not burn effectively.

If testing identified a viable explosive substance, the forensic examiner will usually report the type of explosive rather than identify specific brands. For example, a forensic report will typically identify a material as 'black powder' rather than 'Elephant®' or 'Goex®' brand black powder. For commercial explosives like emulsions or dynamite that are packaged in their original wrapper, a more categorical identification can be made. When identifying an explosive material, the precise identification made will depend largely on laboratory protocol and the type of substance identified. Molecular explosives such as TATP, HMTD, ETN, and NG are relatively simple to report; for example, 'Item 1 contained triacetone triperoxide (TATP).' When oxidizer/fuel mixtures are encountered, reporting can get more complicated. For example, a relatively simple mixture of finely ground potassium perchlorate and aluminum could be identified as any of the following:

- Flash powder;
- Pyrotechnic mixture;
- Perchlorate explosive mixture;
- Perchlorate explosive mixture containing potassium perchlorate and aluminum.

In instances where the material is identified as non-explosive, the identity of the material can still provide important investigative information. The substance may be a precursor material for an explosive mixture or a substance completely unrelated to the manufacture of explosives. As such, reporting the identity of the substance, rather than simply reporting 'no explosives' can be useful. The common uses\properties may be commented on, as above, to give the investigator\court an idea as to the possible sources of said material.

Ultimately, the examiner's responsibility is to provide accurate, authoritative, unbiased information to the investigators\court to aid in due process.

7.6 Questions

1. Explain the term 'intact explosive.'
2. Define what a low explosive is and give two examples.
3. Describe an appropriate analysis scheme for the identification of black powder.
4. What is meant by single, double, and triple base smokeless powders?
5. What analysis techniques could be used to identify a mixture of potassium perchlorate, sulfur, and aluminum? What would that mixture be called?
6. List the three categories of high explosives and give two examples of each.
7. What is meant by a 'molecular' high explosive? Draw two such structures.
8. How should dynamites be packaged for submission to the forensic laboratory?
9. What is a presumptive test and which ones are most commonly used by the forensic examiner?

References

1. Meyer R, Kohler J, Homburg A (2017) Explosives, 6th edn. Wiley-VCH, Weinheim
2. Crippin JB (2006) Explosives and chemical weapons identification. CRC Press Taylor & Francis, New York
3. List of Explosives Materials. Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF) Department of Justice. 28 Oct 2013. Available via https://www.atf.gov/file/97716/download. Accessed 16 Sep 2018
4. Lancaster R (1992) Fireworks principles and practice, 2nd edn. Chemical Publishing Company Inc., New York
5. Russell MS (2008) The chemistry of fireworks, 2nd edn. RSC Publishing, Cambridge
6. Doulan JE, Langer SS (1996) Explosives in the service of man: Ardeer and the Nobel Heritage. TSO, London
7. Routon BJ, Kocher BB, Goodpaster JV (2011) Discriminating HodgdonPyrodex®and Triple Seven®using gas chromatography-mass spectrometry. J Forensic Sci 56:194–199
8. Bottegal M, Lang L, Miller M, McCord B (2010) Analysis of ascorbic acid based black powder substitutes by high-performance liquid chromatography\electrospray ionization quadrupole time-of-flight mass spectrometry. Rapid Commun Mass Spectrom 24:1377–1386
9. Naouum PP, Montgomery E (1928) Nitroglycerine and nitroglycerine explosives. Baltimore Williams and Wilkins Co., Baltimore
10. Smokeless Powder Database. Technical/Scientific Working Group for Fire and Explosions/ National Center for Forensic Science (T/SWGFEX/NCFS). Available via http://www.ilrc.ucf.edu/powders/. Accessed 16 Sep 2018
11. Akhavan J (2004) The chemistry of explosives, 2nd edn. Royal Society of Chemistry, Cambridge
12. Thurman JT (2017) Practical bomb scene investigation, 3rd edn. CRC Press, Boca Raton
13. Army Field Manual FM 5-25. Explosives and demolitions. Department of the United States of America War Office, May 1967
14. ASTM E2998-16 (2016) Standard practice for characterization and classification of smokeless powder. ASTM International, West Conshohocken, PA, www.astm.org
15. E2999-17 (2017) Standard test method for analysis of organic compounds in smokeless powder by gas chromatography-mass spectrometry and fourier transform infrared spectroscopy. ASTM International, West Conshohocken, PA, www.astm.org
16. Yinon J, Zitrin S (1993) Modern methods and applications in analysis of explosives. Wiley, West Sussex
17. Beveridge A (2012) Forensic investigation of explosions, 2nd edn. CRC Press, Boca Raton
18. Oxley JC, Marshall M, Lancaster SL (2012) Principles and issues in forensic analysis of explosives. In: Kobilinsky (ed) Forensic chemistry handbook. Wiley, Hoboken, pp 23–39 (Chapter 2)
19. Houck MM (ed) (2015) Section 5: Explosives. In: Forensic chemistry advanced forensic science series. Elsevier, Amsterdam
20. Saferstein R (2002) Forensic science handbook, vol 1, 2nd edn. Prentice Hall, Upper Saddle River
21. Goodpaster J, Siegel JA (eds) (2016) Chap. 5: Explosives. In: Forensic chemistry fundamentals and applications. Wiley Blackwell, Hoboken
22. Recommended Guidelines for Forensic Identification of Intact Explosives. The technical and scientific working group on fire and explosion analysis (T/SWGFEX) 2004. Available via https://www.swgfex.com/publications. Accessed 16 Sep 2018
23. Explosives Database. University of Rhode Island. Available via http://expdb.chm.uri.edu/. Accessed 16 Sep 2018
24. Feigl A (1972) Spot tests in inorganic analysis, 6th edn. Elsevier, Amsterdam
25. Jungreis E (1996) Spot test analysis: Clinical, environmental, forensic and geochemical applications, 2nd edn. Wiley, Hoboken

26. Lange NA (1971) Spot tests for explosives and explosive residues. Handbook of chemistry, 10th edn. McGraw Hill, New York
27. MacCrehan WA, Reardon MR (2002) A qualitative comparison of smokeless powder measurements. J Forensic Sci 47:996–1000

Hazel Hutson (nee Cullum) is a Principal Case Officer with over 24 years' experience in the forensic examination of items for features of explosives significance. She specializes in trace and bulk explosive analysis, device reconstruction, and provision of expert evidence to the courts. Her published research topics include surveys of high explosives traces in public places, environmental surveys relating to improvised and emulsion/gel explosives, and evidence remaining after the explosion of large improvised bombs. She also regularly provides input to training courses for crime scene examiners, police, and explosive ordnance disposal officers.

Eamonn McGee is a Forensic Chemist at the Centre of Forensic Sciences in Toronto, Canada, with expertise in the forensic analysis of explosives and their residues. He provides scientific support to bomb squads and CBRN teams that includes training in on-site analysis, reach back and scene attendance. He also supports explosive canine training and delivers workshops on homemade explosives and post-blast scene response.

Chapter 8
Explosive Analysis: Introduction to Post-Blast Analysis

B. M. Crane Calhoun and R. F. Mothershead II

Learning Objectives

- Understand scene collection and initial processing of evidence used to select an appropriate analytical scheme.
- Understand analytical schemes and instrumentation for analyzing inorganic and organic explosive evidence.
- Develop awareness of quality control procedures needed to eliminate or account for contamination.

8.1 Introduction

Post-blast analysis involves the chemical identification/determination of residual explosive compounds and/or the reaction products formed as the result of an explosion. Due to the destructive nature of an explosion, the examination of post-blast evidence is focused typically on the recovery and analysis of residues or trace levels of relevant compounds.

A post-blast scene can range from small and localized (e.g., a pyrotechnic device exploding in a mailbox) to an expansive debris field with extensive damage (e.g., the 1995 bombing of the U.S. Federal building in Oklahoma City, Oklahoma). The proper collection of best evidence for chemical testing in a forensic laboratory

---

B. M. Crane Calhoun (✉)
Bureau of Alcohol, Tobacco, Firearms and Explosives-Forensic Science Laboratory,
Walnut Creek, CA, USA
e-mail: brittany.crane@atf.gov

R. F. Mothershead II
Federal Bureau of Investigation Laboratory, Quantico, VA, USA
e-mail: rfmothershead@fbi.gov

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_8

requires a logical and systematic approach based on the understanding of the chemistry and physics involved in an explosion created by chemical reactions. Specialized training is required for crime scene personnel assisting with a post-blast scenario.

Generation of reliable data that can be used for valid scientific interpretation begins with collection practices at the scene. Field collection of evidence suitable for post-blast chemical analysis focuses on two main types of evidence. Physical items are the first type, which may be either directly associated with the explosive device or objects in the immediate vicinity of the explosive and may have chemical residues present on them. Examples include device components, containers, added enhancements (e.g., ball bearings, nails; to be discussed further in Chap. 9), clothing, and items damaged as a result of close proximity to the seat of the explosion. If these items can be easily collected and packaged, then they should be sent directly to the laboratory for chemical testing and any other probative forensic examinations. Ideally, packaging would be vapor tight (e.g., lined paint can with lid), but plastic bags and glass vials/jars generally are also sufficient. It should be noted that if the evidence is submitted in containers that are not vapor tight, the potential exists for the loss of volatile chemicals from the evidence. These vapors may also potentially contaminate evidence in close proximity.

The second type of evidence collected on scene consists of articles used to remove chemical residues from the surface of items that are too large or cumbersome to send directly to the laboratory. These residues are recovered by wiping (swabbing) the selected surface with an absorbent material such as a cotton ball or gauze pad, then placing the swab into a proper packaging for transport to the laboratory [1]. The absorbent material (swab) may be dry or wetted with a solvent such as water or alcohol. This technique works best on non-porous surfaces such as metal or glass. Examples of items commonly swabbed on scene include street signs, vehicle surfaces (exterior and interior), table or bench tops, and damaged building edifices. An alternative collection technique for explosive residues from porous items such as cloth or carpet is vacuuming of the evidence item onto designated vacuum filters or adsorbent tubes, which are then submitted for laboratory analysis. While these collection techniques are acceptable, the submission of the actual item is preferable.

Quality control (QC) measures are critical during field collection for post-blast residues to prevent and/or monitor possible contamination. At a minimum, clothing and gloves must be changed before sampling other post-blast or search scenes. Any collection tools such as tweezers, shovels, and brushes should be disposable or cleaned between items gathered. Unused swabbing material from the same lot or batch used for evidence collection should be packaged on scene and submitted as control samples in similar packaging. If a solvent is used to wet the swab material before collection, the control swab should be treated in a similar fashion. Additional QC samples can include swabbings taken of the gloves and clothing used by field personnel prior to collecting evidence.

As discussed in Chap. 7, explosives can be classified into different categories based on their intended use or alternatively can be separated into high or low

Table 8.1 Commonly encountered organic explosives

Nitrate Esters (–O–NO_2)	Nitroaromatics (Ar–NO_2)
Ethylene glycol dinitrate (EGDN) Nitrocellulose (NC) Nitroglycerin (NG) Pentaerythritol tetranitrate (PETN) Erythritol tetranitrate (ETN)	Dinitrotoluene (DNT) isomers Trinitrotoluene (TNT) Picric acid
Nitramines (–N–NO_2)	Peroxides (–O–O–)
RDX HMX	TATP HMTD

explosives based on their rate of reaction. Another way of grouping explosives is the elemental composition and/or molecular structure, with most explosives being classified as either organic or inorganic materials. Because different types of instrumental methods are typically used for organic and inorganic analyses, grouping explosives in this way helps the examiner select an appropriate analytical scheme.

Organic explosives are monomolecular carbon-based compounds that also contain other elements such as oxygen, nitrogen, and hydrogen. Typical classes of organic explosives include **nitroaromatics**, **nitramines**, **nitrate esters**, and solid **peroxide** compounds, such as triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) (Table 8.1).

Inorganic explosives generally do not have carbon-based constituents and include various mixtures with nitrate, chlorate, or perchlorate salts (e.g., ammonium nitrate, potassium perchlorate) as the oxidizer (Table 8.2). Some inorganic explosive materials may have organic compounds as a fuel (e.g., ascorbic acid in select black powder substitutes).

The reaction products of organic explosives tend to be gases, with very little solid residues. Therefore, analysis for organic explosives focuses primarily on any traces of unreacted explosive left behind. Most inorganic explosives, on the other hand, often produce solid reaction products in addition to any gases formed. The analysis for inorganic explosives involves identifying these solid reaction products as well as any unreacted residual material. In general, the organic explosives are more soluble in non-aqueous solvents, such as dichloromethane or acetone, while some constituents of the inorganic explosives and their reaction products dissolve in water. As such, different analytical approaches are needed for the identification of the residues from various explosive materials.

Table 8.2 Commonly encountered inorganic explosives

Explosive (Oxidizers)
Black powder (potassium nitrate)
Pyrodex® (potassium nitrate, potassium perchlorate)
Triple Seven®(potassium nitrate, potassium perchlorate)
Pyrotechnic Compositions (nitrates, chlorates, perchlorates)

8.2 Post-Blast Analysis of Explosives

As important as it is to adopt **contamination** prevention procedures during evidence collection, it is equally necessary to follow good laboratory practices while processing evidence for residues of explosives to minimize and monitor any potential intra-laboratory contamination. A comprehensive quality assurance program will encompass the preparation of proper negative controls during evidence examinations that account for all solvents, reagents, and supplies used in the processing of the evidence. Quality assurance practices for trace explosive analysis may also include monitoring laboratory examination space and immediate environment for potential contamination [2, 3].

8.2.1 Visual and Microscopical Examination

Regardless of the type of evidence submitted or the chemical classification of the involved explosive, the first step in any post-blast analysis is to look at the evidence up close, with the naked eye and under magnification, which will assist the examiner in developing an analytical strategy. Certain explosives (e.g., black powder) produce substantial solid reaction products which may be deposited on objects such as the containers that enclosed the explosive when it initiated. A visual inspection of collected evidence may indicate selected items or areas on an item (e.g., with soot deposits) that are most likely to yield chemical information regarding explosives employed. It is important to note to minimize the amount of time conducting a visual inspection to avoid loss of more volatile compounds (e.g., EGDN).

A careful visual inspection of evidence items under a microscope may reveal particles or grains of potential uninitiated explosive material suitable for analysis (Figs. 8.1 and 8.2). Any visible residues are collected by an effective method such as scraping or removal with tweezers. If a sufficient amount of residue is present, it may be analyzed using the same instrumentation as intact explosives (e.g., SEM-EDS, FTIR, XRD; see Chap. 7). The recognition through visual or microscopical inspection of small particles or grains with morphology or features characteristic of specific types of explosive compositions as described in Chap. 7 (e.g., smokeless powders) can also assist the examiner in reaching a more definitive conclusion about any chemical residues identified.

The absence of visible residues on evidence items that exhibit damage associated with being near the seat of an explosion may also indicate the potential use of specific explosives that produce little to no solid residue upon initiation. For example, the solid peroxide-based explosives TATP and HMTD react to produce only gaseous products and leave behind no visible residue attributed to the explosives themselves. Even smokeless powders may leave little to no residue when fully consumed.

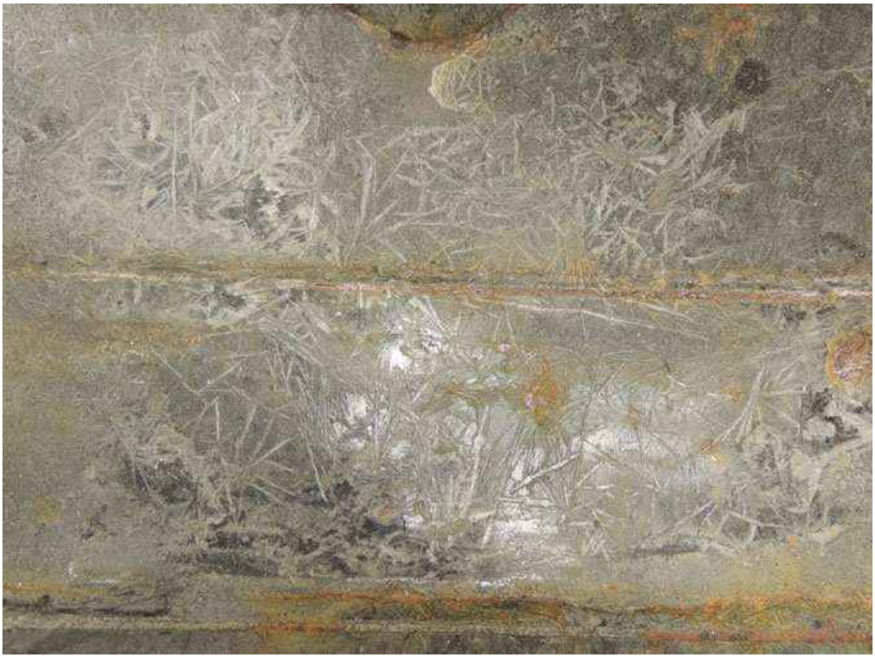


Fig. 8.1 Post-blast ammonium nitrate crystals on metal

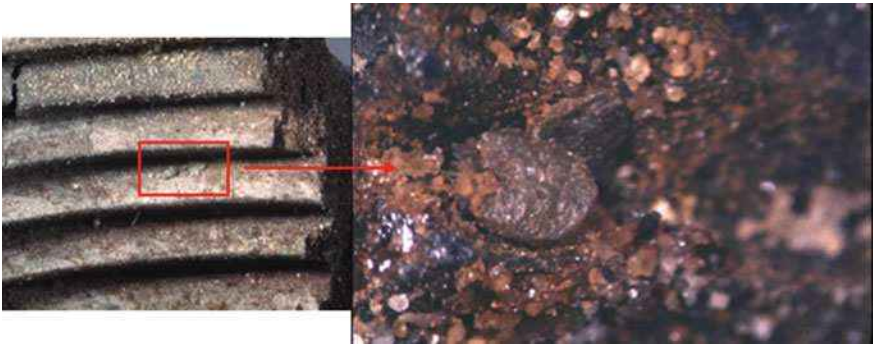


Fig. 8.2 Smokeless powder particle among debris embedded in pipe threads. Photographs courtesy of Edward Bender

While examining the evidence macroscopically, damage to the evidence should be assessed. Are the items of evidence large or small (e.g., pipe fragments)? Is there residue present? Do metal fragments exhibit any damage characteristic of some high explosives (e.g., pitting, blueing)? These observations are noted, as they are indications of what type of explosive may have been used.

If the visual and microscopical examination has been conducted, and no visible, removable residues have been observed, the next step is to isolate or extract potential trace explosives from the evidence items for analysis. Typically, the items will first be treated to remove organic residues, then inorganic residues, unless the solvent is chosen such that the extraction is performed simultaneously.

8.3 Post-Blast Analysis of Organic Explosives

If an organic explosive is suspected, the explosives may be isolated using a vapor sampling technique or extracted with a solvent, such as acetone, ethanol, dichloromethane, methanol, or isopropanol, for a sufficient time to dissolve the explosive compounds into the solvent. Alternatively, a mixed solvent (e.g., an alcohol and water) can be used for extraction and apportioned for both organic and inorganic explosive analyses. Organic extracts can be evaporated gently to remove excess solvent and concentrate any extracted compounds.

Many other compounds in addition to explosive-related chemicals may be present on evidence items recovered from a post-blast scene, including dirt, grease, soot, and even blood. As a consequence, solvent extracts may need to be processed through a clean-up step prior to instrumental analysis. Removing extracted contaminants from the sample matrix will assist with method sensitivity and selectivity as well as reduce instrument fouling. Techniques such as syringe filtration and solid phase extraction (SPE) have been used to clean-up complex extracts such as soil and oily swabs [4–7]. SPE involves trapping organic molecules onto a solid adsorbent phase, typically within a disk or cartridge, while letting other non-retained compounds in the extract pass through the adsorbent. The analytes of interest are then removed by rinsing the SPE media with a strong organic solvent.

Alternate extraction techniques can be applied to improve selectivity by reducing the number of co-extracted compounds from a sample. Adsorption techniques such as charcoal strips and solid phase microextraction (SPME), as discussed in Chap. 2, have been used successfully to adsorb explosives directly from water-based extracts as well as vapors of more volatile explosives released from gently heated evidence items [8–11].

After the sample has gone through any necessary filtration and clean-up steps, it is ready for instrumental analysis.

8.3.1 Instrumental Analysis

Once potential organic explosive residues have been isolated, the next steps in post-blast analysis are detection and identification of any analytes of interest in the samples. This often starts with an initial screening technique to provide a presumptive indication of which samples have possible explosives in them. For post-blast scenes with many submitted samples, this step can help reduce the number of samples that need to proceed to confirmatory analysis. Screening techniques for organic explosive residues typically involve gas or liquid chromatography coupled with detection such as chemiluminescence, electron capture, or photodiode array. These detectors are chosen due to their selectivity for chemical properties common to many organic explosives, such as the presence of nitrogen-containing functional groups, electronegative moieties, or aromatic features. The use of chromatography allows for the separation of potential explosives from the remainder of the "chemical soup" in the solvent extract. Ideal screening methods should be rapid and sensitive in order to quickly determine the most probative samples to pursue further. Ion Mobility Spectrometry (IMS) is a rapid and sensitive screening technique used for decades at transportation hubs, such as airports, to check for explosive residues on luggage and personnel. While its use in the laboratory setting to quickly evaluate items for traces of explosives has been reported [12–14], IMS has significant disadvantages including oversaturation and often conveying false positives and, therefore, is not commonly used in forensic laboratories.

Screening tests can provide preliminary information about samples, but for final identification, samples with suspected explosives must be analyzed by a definitive technique. Confirmatory analysis of organic explosive residues usually involves chromatography coupled to a structural elucidation technique, the most common being mass spectrometry.

GC-MS with electron ionization (EI) is used most often for residues of smokeless powder constituents such as organic additives (e.g., diphenylamine, methyl or ethyl centralite, phthalate esters). Residues of the improvised explosive TATP have also been analyzed using SPME with GC-MS (EI). Certain organic explosive structural groups, such as the nitrate esters, fragment readily under EI conditions, yielding no molecular ion (Fig. 8.3).

As discussed in Chap. 1, GC-MS with negative ion chemical ionization (NICI) is a softer ionization technique that generally favors the production of a molecular ion with reduced mass fragmentation. NICI is highly sensitive for electronegative compounds and has been used successfully for the stand-alone identification of nitroaromatics such as trinitrotoluene (TNT) and dinitrotoluene (DNT) isomers (Fig. 8.4). It is also a good supplemental technique for the identification of nitroesters.

LC-MS utilizing either ESI or APCI is effective for a wide range of organic explosives. LC-MS generally incorporates a softer ionization technique, allowing for better molecular weight information than GC-MS for labile compounds. In addition, some explosives may require the use of mobile phase additives (e.g., ammonium acetate, ammonium nitrate) to ensure proper ionization (Fig. 8.5). The most common operation mode for the LC-MS is full scan mode; however, other modes such as tandem mass spectrometry (MS/MS) have seen increased application to explosive analysis [15, 16].

In recent years, the commercial availability of high-resolution mass spectrometers has led to increased use of this instrumentation to improve specificity and

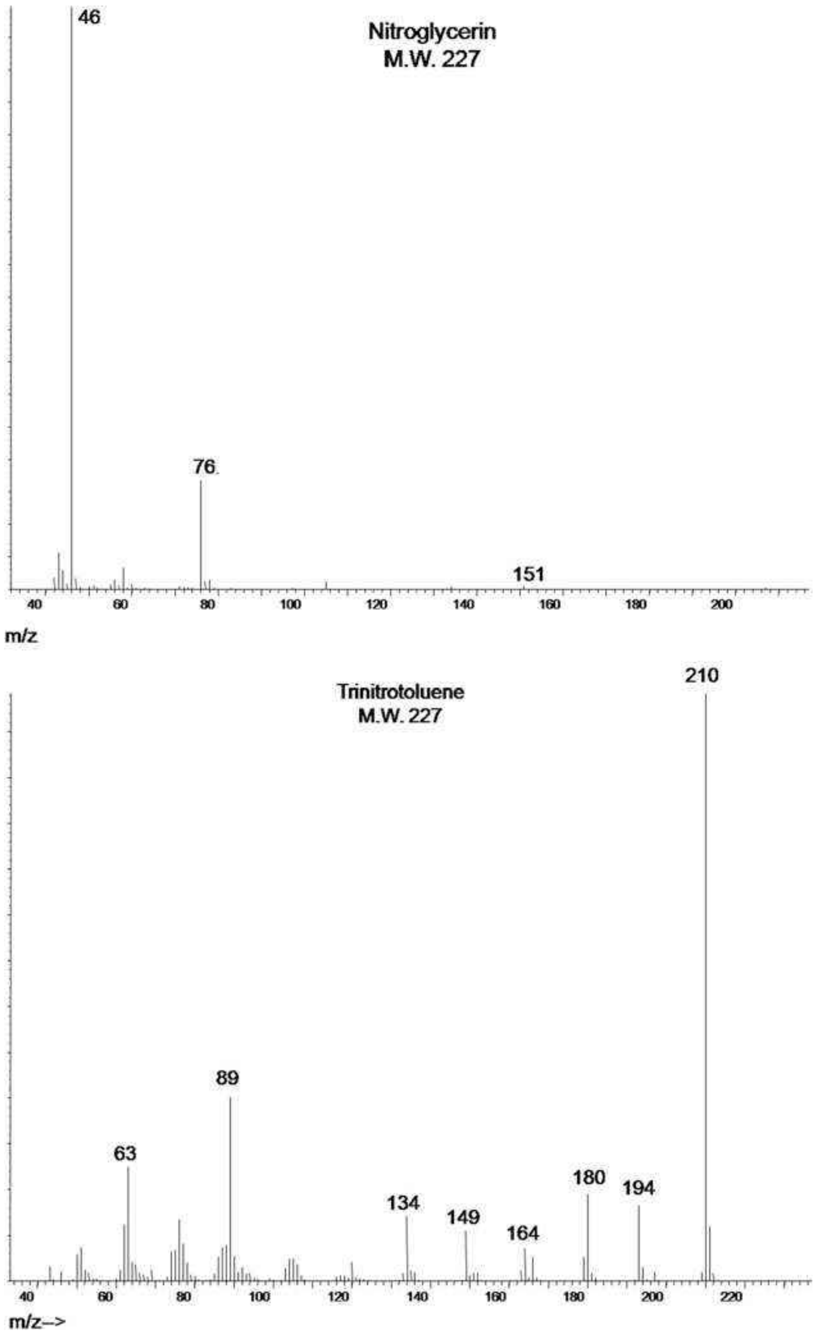


Fig. 8.3 EI mass spectra of nitroglycerin (nitrate ester) and trinitrotoluene (nitroaromatic). Both compounds have a nominal molecular weight of 227

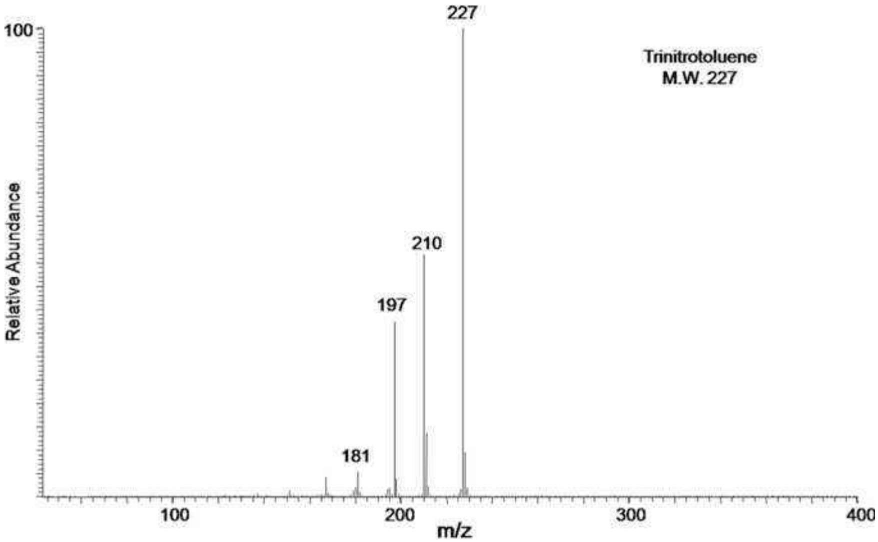


Fig. 8.4 NICI mass spectrum of trinitrotoluene (TNT)

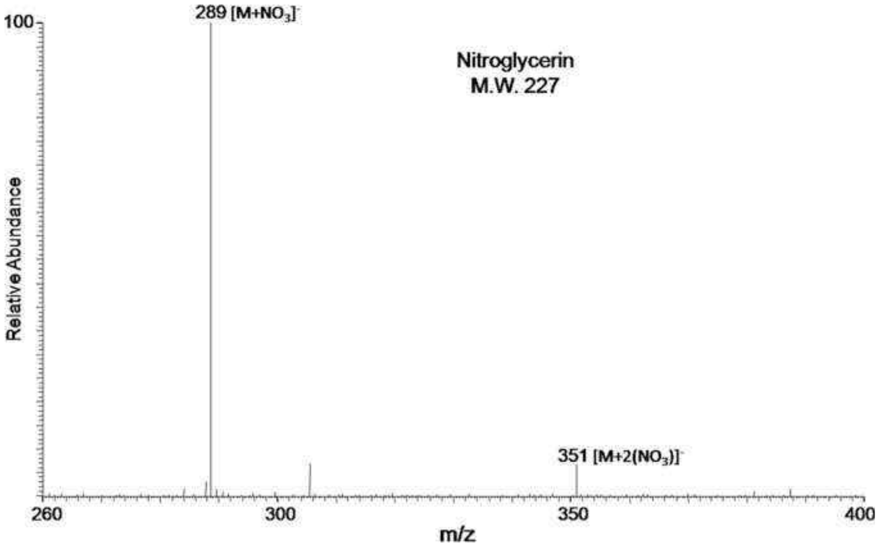


Fig. 8.5 LC-MS-ESI mass spectrum of nitroglycerin (NG) with nitrate adduct (M.W. 289)

sensitivity for organic explosive analysis [16]. Techniques such as time-of-flight (TOF) mass spectrometry coupled to interfaces such as desorption electrospray ionization (DESI) or direct analysis in real time (DART) have allowed compound separations to be achieved based on mass resolution, thus minimizing the need for traditional chromatographic techniques. This approach offers increased speed of analysis, selectivity, and sensitivity [17, 18]. High-resolution mass spectrometry is especially useful when coupled with chromatography. As the affordability of high-resolution mass spectrometers improves and more validation studies on its application to explosive analysis are published, the presence of these analytical tools should become more widespread in forensic explosives laboratories.

Identification of a chemical for a forensic report typically includes at least two positive test results for the analyte of interest using separate test procedures. Ideally, at least one of the test methods involves a structural elucidation technique (e.g., spectroscopy or mass spectrometry). The use of multiple techniques that approach the analyte from “different angles” is often referred to as orthogonal testing, as discussed in Chap. 7. Provided that there is sufficiently complex spectral information, a single hyphenated instrument, such as GC-MS, may be sufficient. It can also be as simple as analyzing the same mixture by GC-MS on columns with two different chemistries, such that the retention order would be expected to change. Alternatively, the same instrument can be used, but with two different ionization methods.

8.4 Post-Blast Analysis of Inorganic Explosives

As an inorganic explosive undergoes a chemical reaction (i.e., an explosion), solid reaction products form which can be the targets of analysis. An example of this type of reaction is black powder [19]:

$$10KNO_3 + 8C + 3S \rightarrow 3K_2SO_4 + 2K_2CO_3 + 6\ CO_2 + 5N_2$$

The post-blast products (K_2SO_4 and K_2CO_3 in the example) are often visible residues that can be scraped from the surface and analyzed relatively simply. Other reaction products result from the decomposition of a reactant as observed with explosives containing a perchlorate salt. For example, potassium perchlorate decomposes to potassium chloride and gaseous oxygen with the solid product amenable to identification. Table 8.3 lists possible reaction products that may be detected/identified in analysis of residues for commonly encountered inorganic explosives; some unreacted components may also be present. The utility of FTIR for making identification of components is limited due to mixtures of reaction products.

If no residue is visible or a sufficient amount cannot be collected, a solvent extraction is conducted to collect any trace amount of inorganic explosives that may be present. Deionized water is the appropriate solvent for extraction due to the water solubility of many of the components from inorganic explosives. Hot water in particular is useful due to the increased solubility of compounds such as potassium chlorate and perchlorate [21], and extraction efficiency can be improved by using

Table 8.3 Some possible post-blast components of visible residues from inorganic explosives detected/identified by SEM-EDS, FTIR, and XRD [20]

Explosive	Unreacted components	SEM-EDS	XRD and/or FTIR
Black Powder	KNO_3, S, C	O, S, K	K_2SO_4, K_2CO_3
Pyrodex®	KNO_3, $KClO_4$, sodium benzoate, cyanoguanidine, S, C	O, S, K, Cl	KCl, K_2SO_4, K_2CO_3
Triple Seven®	KNO_3, $KClO_4$, sodium benzoate, cyanoguanidine, sodium 3-nitro-benzoate, C	O, K, Cl	KCl, K_2CO_3
Black MZ™	KNO_3, $KClO_4$, ascorbic acid, C	O, K, Cl	KCl
$KClO_4$/Al mixture	$KClO_4$, Al	O, Al, Cl, K	KCl, $KClO_3$, Al_2O_3

sonication. Typically, most of the extract is evaporated to recover any residue, while a portion is retained for ion analysis.

An important aspect to preparing and analyzing extracts is to have a method blank of the solvent used for extraction to ensure that any ions identified are actually from the sample. This quality procedure becomes even more important when dealing with the extractions of swabs. A control swab is highly recommended to ensure any ions identified are not from the swab material. This is important because of the ubiquitous nature of many ions and will determine the consideration given to ions from the environment and/or collection materials. Additionally, the preparation of the extracts needs to be performed carefully, as targeted ions could be in the environment. For example, the use of a glass vial to store a water extract will cause leaching of sulfate ions from the glass into the extract, potentially minimizing the appearance of other ions in the final IC data.

Similar to post-blast analysis of organic explosives, extracts need to go through a clean-up procedure, such as filtration, in which extraneous particles and debris are eliminated in order to increase the signal of the sample. The extent of the clean-up depends on the sample matrix, the detector, and sensitivity of the instrument being used (e.g., HPLC versus IC-MS).

8.4.1 Instrumental Analysis

Water extractions, now isolated and prepared, are analyzed by chromatographic separation techniques often coupled with confirmatory techniques such as mass spectrometers (e.g., IC-MS, LC-MS).

As discussed in Chap. 1, ion chromatography (IC) is a common separation technique which utilizes conductivity detection to screen for post-blast inorganic explosives. Different types of analytical columns may be used as long as there is good resolution and peak shape for the ions of interest. Multiple columns may also need to be used in order to cover all of the targeted ions. IC is frequently coupled with mass spectrometry to create a confirmatory technique. Due to the sensitivity of the MS, the samples may need to be diluted based on their conductivity and filtered using a syringe filter. Depending on what ions are identified, the broad type of the original explosive may be refined.

The most commonly encountered anions of interest associated with inorganic explosives are chloride, nitrite, nitrate, chlorate, benzoate, and perchlorate which can be identified using IC-MS (Figs. 8.6 and 8.7). Sulfur-containing mixtures can also produce sulfate, thiosulfate, and thiocyanate ions (Table 8.4). Ascorbic acid-based black powder substitutes are also recognizable since IC-MS can be used to identify three degradation products of ascorbic acid: monohydrated diketogulonate (m-DKG), oxalate, and threonate (Fig. 8.8) [22, 23]. However, the analysis of ascorbic acid-based black powder substitutes by IC-MS may be challenging due to chromatography restrictions and post-blast situations. The detection of cations may also be useful in determining possible oxidizers or fuels but may not be as probative as anion analysis. The cations of interest most commonly encountered are sodium, ammonium, potassium, magnesium, calcium, strontium, and barium. Cation detection may not be routinely conducted if a laboratory has the capabilities of identification of salts using techniques such as FTIR and/or XRD.

The benefits of IC-MS for post-blast analysis are demonstrated by its ability to differentiate between residues of black powder and black powder substitutes (Fig. 8.9). Post-blast black powder may yield nitrite, nitrate, sulfate, and thiocyanate ions. Black powder substitutes, which contain potassium perchlorate in the formulation, may yield residues that include chlorate and perchlorate anions. Depending on the original formulation of the black powder substitute, sulfate, thiosulfate, and benzoate ions may also be identified and can help distinguish between different types of black powder substitutes, like Pyrodex® and Triple Seven® (as discussed in Chap. 7). Sodium 3-nitrobenzoate, which converts to 3-nitrobenzoic acid (3-NBA) in water, can also be added to the standard in order to differentiate between Pyrodex® and Triple Seven®.

LC techniques, which may or may not be coupled with a mass spectrometer for confirmation, may be used in post-blast analysis of inorganic explosives. HPLC is useful in the differentiation between Pyrodex® and Triple Seven®. The compounds of interest are cyanoguanidine, 3-NBA, and benzoic acid. Benzoic acid forms from sodium benzoate in water in a similar fashion as 3-NBA, as discussed earlier. Each compound absorbs light in the UV region allowing detection by the photodiode array. LC, when coupled with an MS, has shown capabilities of detecting anions related to degradation products from ascorbic acid-based black powder substitutes [24]. Another chromatographic technique that may be used is CE. If a confirmatory technique such as MS is not used, CE can serve as a complementary technique to IC [25, 26]. It is important to note, however, that neither CE nor IC can be used as a stand-alone identification without a coupled confirmatory technique.

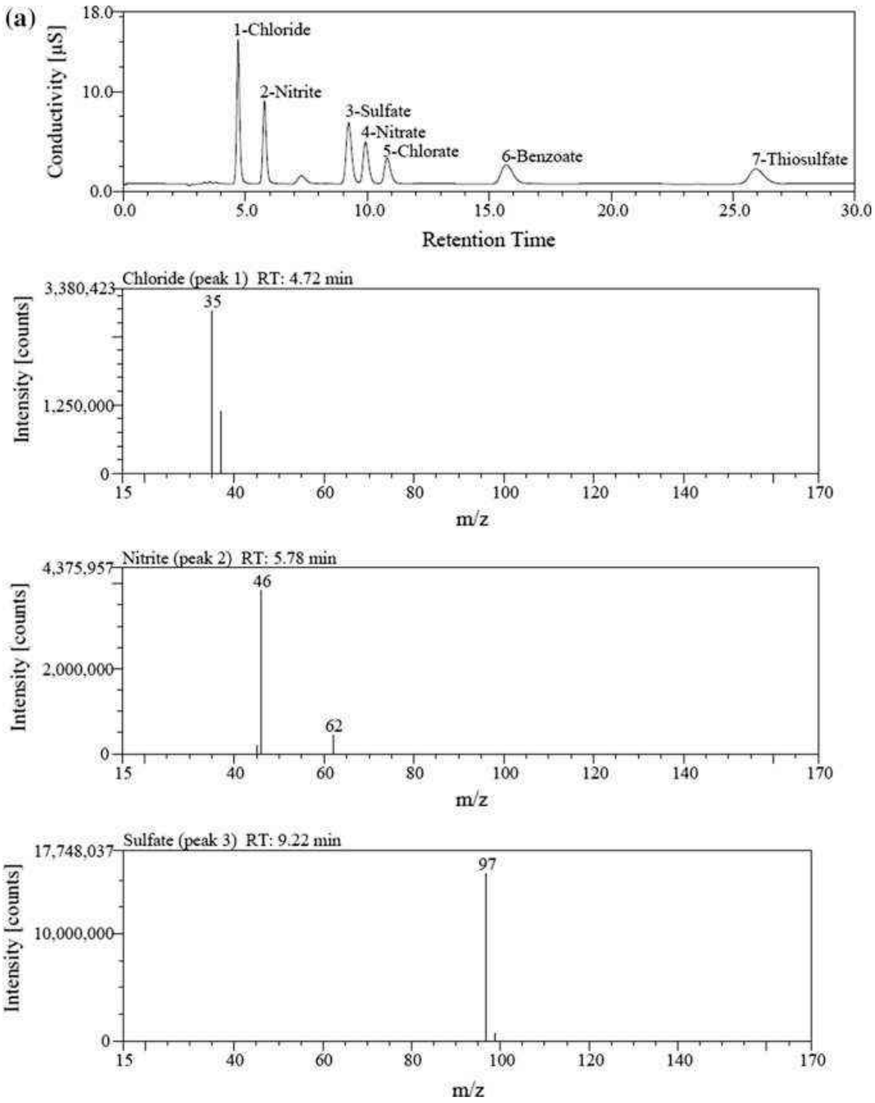


Fig. 8.6 Ion chromatograms of anion standards on analytical column AS18, with associated mass spectra for peaks 1–3(**a**) and 4–7(**b**)

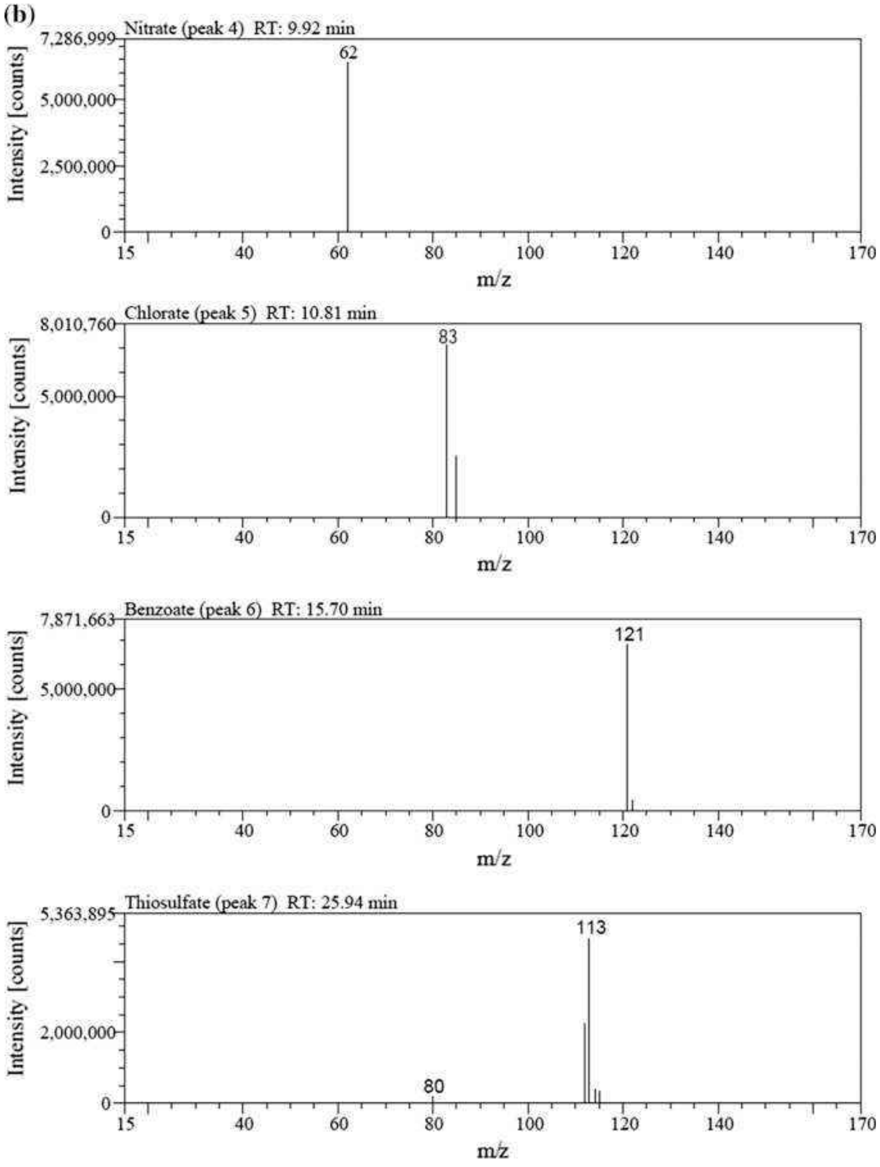


Fig. 8.6 (continued)

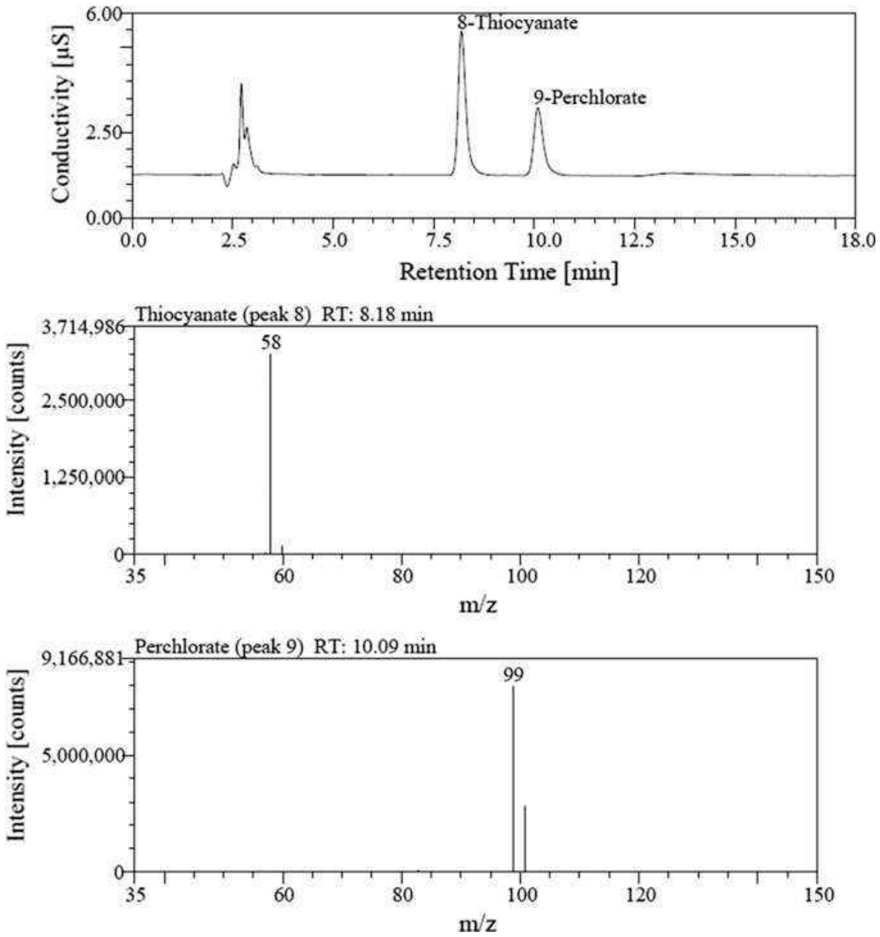


Fig. 8.7 Ion chromatograms of anion standards on analytical column AS16, with associated mass spectra for peaks 8 and 9

Table 8.4 Some possible post-blast anions and compounds from extracts of inorganic explosives detected/identified by IC-MS and HPLC [20]

Explosive	Unreacted Components	IC-MS (anions)	HPLC
Black Powder	KNO_3, S, C	NO_2^-, SO_4^{2-}, NO_3^-, $S_2O_3^{2-}$, SCN^-	–
Pyrodex®	KNO_3, $KClO_4$, sodium benzoate, cyanoguanidine, S, C	Cl^-, NO_2^-, SO_4^{2-}, NO_3^-, ClO_3^-, benzoate, $S_2O_3^{2-}$, SCN^-, ClO_4^-	Cyanoguanidine, benzoic acid
Triple Seven®	KNO_3, $KClO_4$, sodium benzoate, cyanoguanidine, sodium 3-nitro-benzoate, C	Cl^-, NO_2^-, NO_3^-, ClO_3^-, benzoate, 3-NBA, ClO_4^-	Cyanoguanidine, 3-NBA, benzoic acid
Black MZ™	KNO_3, $KClO_4$, ascorbic acid, C	Cl^-, NO_2^-, $^-$, NO_3^-, ClO_3^-, ClO_4^-, threonate, m-DKG, oxalate	–
$KClO_4$/Al mixture	$KClO_4$, Al	Cl^-, ClO_3^-, ClO_4^-	–

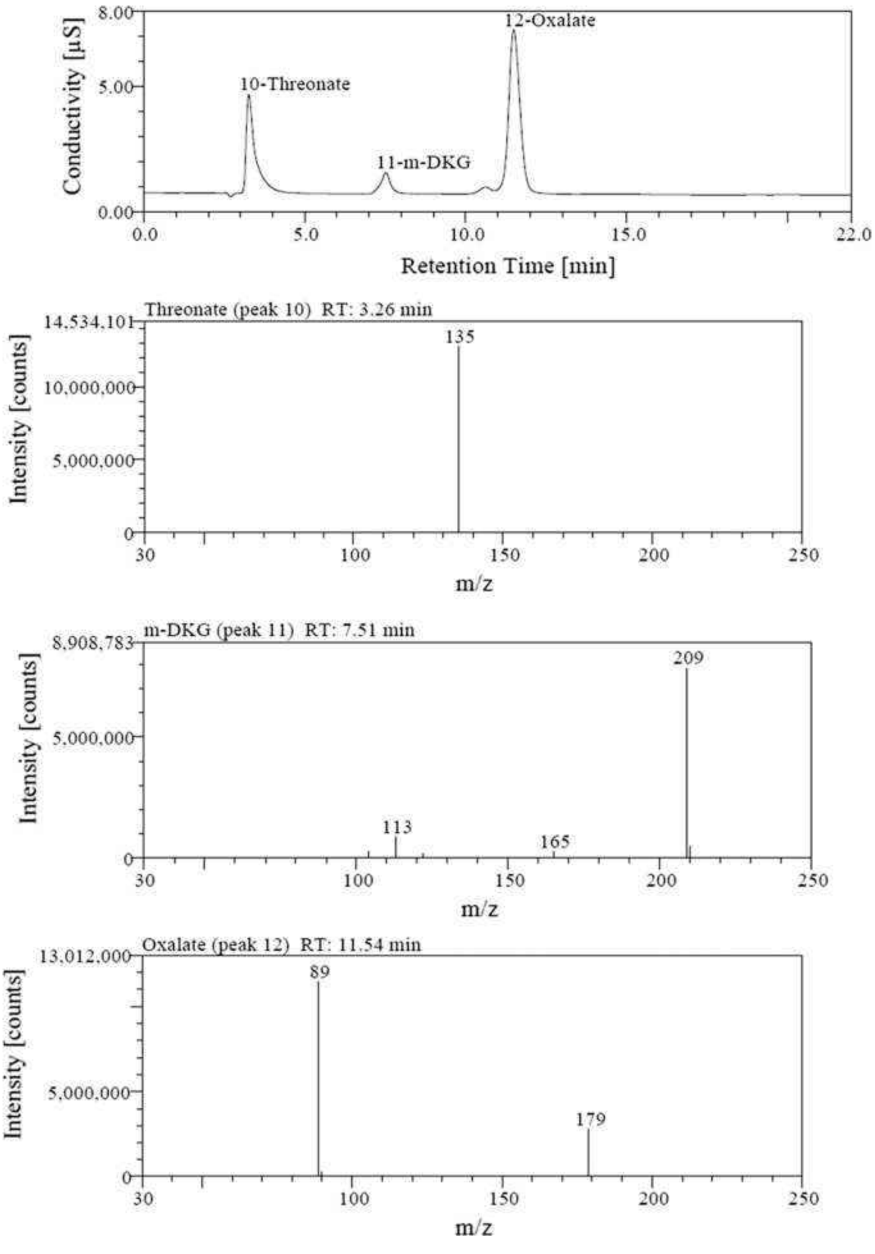


Fig. 8.8 Ion chromatogram of ascorbic acid standard on analytical column AS18, with associated mass spectra for three degradation products (peaks 10–12) of ascorbic acid

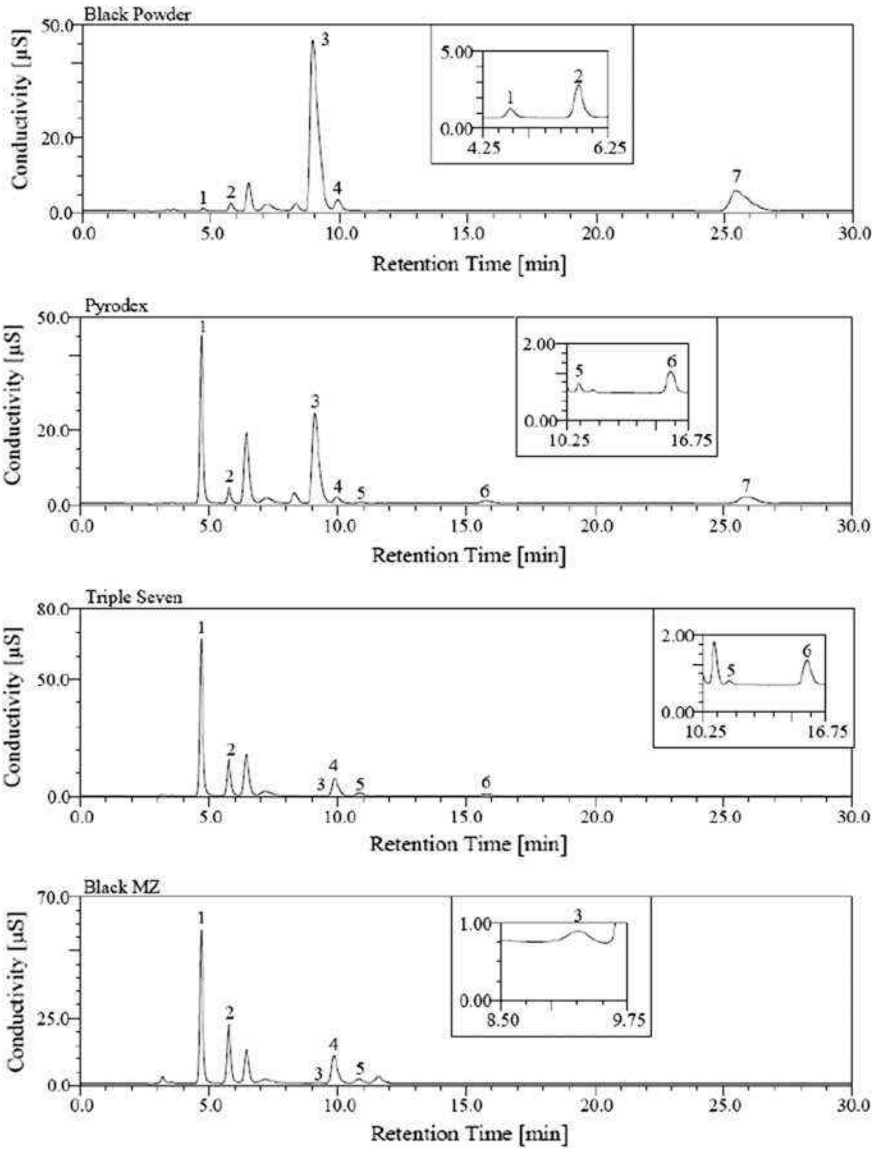


Fig. 8.9 Ion chromatograms of post-combustion Black Powder, Pyrodex®, Triple Seven® and Black MZ™ on analytical column AS18. See Fig. 8.6 for numbered peak assignments

8.5 Interpretation and Reporting of Results

While the analysis of explosive residues from a post-blast crime scene can be time-consuming, the true challenge can arise when the resultant data needs to be interpreted and reported. The responsibility of the forensic chemist is to not only document the results of the chemical testing, but to also explain how the presence of those specific chemicals may relate back to the use of an explosive or explosive mixture.

For all explosive residues, the challenge lies principally in the likelihood of any parent explosive being present on a specific item examined in the laboratory and the likelihood of that particular explosive compound being present in the environment [27–30]. Certain monomolecular compounds, such as TNT or RDX, are almost exclusively produced and used as explosives; therefore, residues of these chemicals have stronger potential correlation to the explosive event. Proper comparison samples from the scene and control samples addressing both field and laboratory work will assist in assigning eventual significance to the presence of these residues. On the other hand, the presence of NG could be a result of its use in an explosive material (e.g., double-base smokeless powder or some dynamites), but it could also originate from other sources (e.g., some heart medications). Where the specific residue is identified can assist with determinations of the significance of its presence. Residues of NG on the inner surfaces of a pipe fragment with indications of explosive damage may be less likely due to non-explosive sources than residues identified on the outer surfaces of such items or on clothing from a person with a history of heart conditions.

For inorganic explosives, the residue may be from unreacted material as well as reaction products, many of which can have multiple sources common to the environment. For example, the presence of potassium, nitrate, chloride, and sulfate ions may be the result of an explosive mixture that includes potassium nitrate, sulfur, and a chlorate or perchlorate component, but these ions could be present on the evidence due to one or more other sources. If an inorganic explosive is placed inside of a device made with polyvinyl chloride (PVC) pipe, a chloride salt could be formed whether the explosive has a chlorine source in it or not [31] resulting in an identification of chloride ions in IC-MS data. Soil samples in particular will have numerous inorganic species (e.g., nitrate, chloride, sulfate, perchlorate) that can complicate the interpretation of residue results [32]. Nitrate salts, for example, are commonly found in fertilizers and some deicing products. The substrate and the relative abundance of various anions must be taken into account during interpretation.

It is also important to know the manufacturing processes for explosives as it may help with interpretation of analytical results. For example, the Vice President of Operations for Hodgdon Powder Company has confirmed that Pyrodex® and Triple Seven® are manufactured with the same equipment (Brad Schick, June 11, 2018). Therefore, it is possible there is a trace amount of sulfur-containing compounds in Triple Seven®, despite the bulk formulation being sulfur-free. As seen in Fig. 8.9, it is possible for sensitive instrumentation to pick up remnants and reaction products resulting from the unintended inclusion of extraneous compounds.

The forensic chemist must consider the compilation of all chemical species found and the nature of the evidence item examined, along with its potential handling and environmental exposure history, in order to provide valid and valuable interpretation to the analytical results.

As with reporting intact explosives, different approaches can be taken to provide various amount of information to the investigator/court. One approach may be to only include analytical results such as ions and compounds identified, without any interpretation. However, this may be confusing or uninformative to a reader without relevant scientific background. To address any confusion, a conclusion could follow in the report to interpret the information for the lay audience. Another approach is to simply provide a conclusion of the type of explosive, if present.

8.6 Summary

Post-blast analysis encompasses the examination of both visible and microscopic residues left behind after an explosive event, focusing on chemical evidence for the explosive material involved. Quality control measures to prevent or minimize

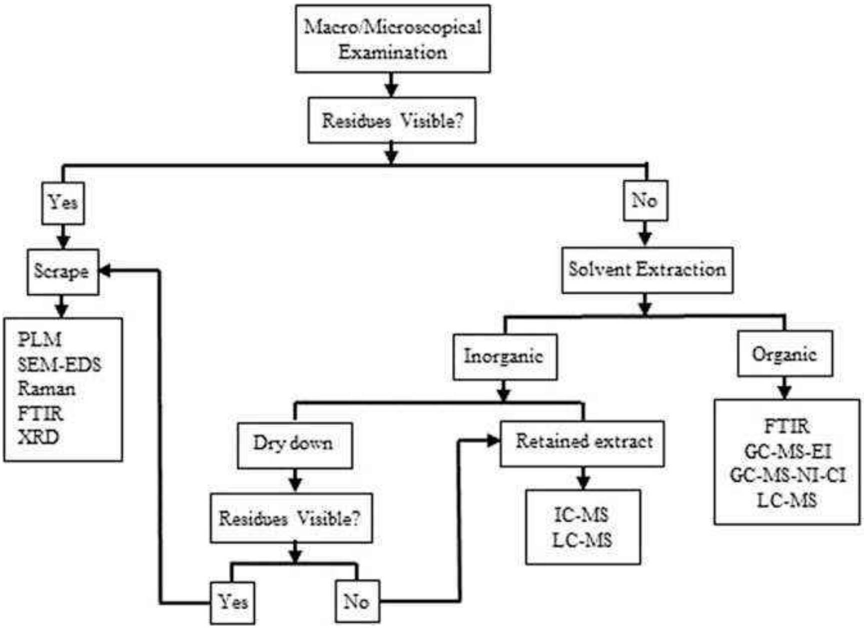


Fig. 8.10 Example of a flowchart for post-blast analysis

contamination of evidentiary items begin during evidence collection and extend through the laboratory examination process. There are a broad variety of techniques and solvents that can be used for the isolation or extraction of post-blast residues, and the method used will vary depending on laboratory protocol and instrumental capabilities. Packaging materials may also indicate what type of techniques are possible (e.g., vapor tight containers allow vapor analysis). Figure 8.10 provides an example of a logical strategy to address a comprehensive analysis with typical instrumentation. Post-blast analysis is not a linear analysis as a combination of inorganic and organic explosives may be used in a device. This is evident in the case studies discussed in the following section.

8.7 Case Studies

8.7.1 Case Study 1 (Post-Blast Analysis for Organic Residues)

Scenario

An explosion occurred at a local business establishment involving a suspected pipe bomb. The device had been placed at the base of a door. The explosion damaged the door and building and sent fragmentation into the surrounding neighborhood. Evidence was located approximately 250 yards from the blast seat. Submitted to the laboratory for analysis were pieces of apparent metal pipe and threaded end caps, all exhibiting extensive damage (Figs. 8.11 and 8.12).

Analytical Results

The metal fragments were inspected, and no visible residues were observed. As such, selected inner surfaces were rinsed with acetone to remove any organic residues and separate inner surfaces rinsed with deionized water to remove

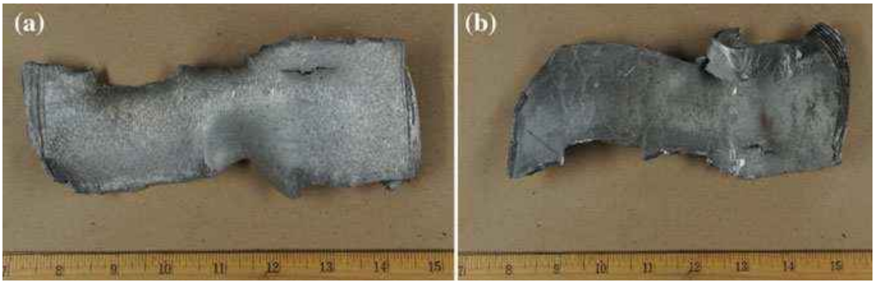


Fig. 8.11 Item 1 large metal piece with threads: **a** inner curvature surface, **b** outer curvature surface. Reference scale is marked as inches

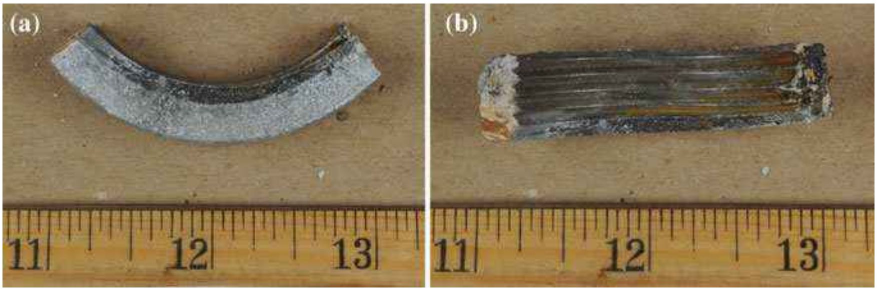


Fig. 8.12 Item 2 small metal piece with threads: **a** edge surface, **b** inner threaded surface. Reference scale is marked as inches

inorganic species. The acetone extracts were analyzed by GC-ECD to screen for explosives and related organic compounds, followed by analysis with GC-MS and LC-MS. Residues of nitroglycerin, diphenylamine, ethyl centralite, and 2,4-dinitrotoluene, common smokeless powder additives, were identified on Items 1 and 2.

Figure 8.13 depicts the GC-ECD chromatogram for the Item 1 acetone extract. The GC-MS-EI total ion chromatogram (TIC) for the Item 1 extract and extracted

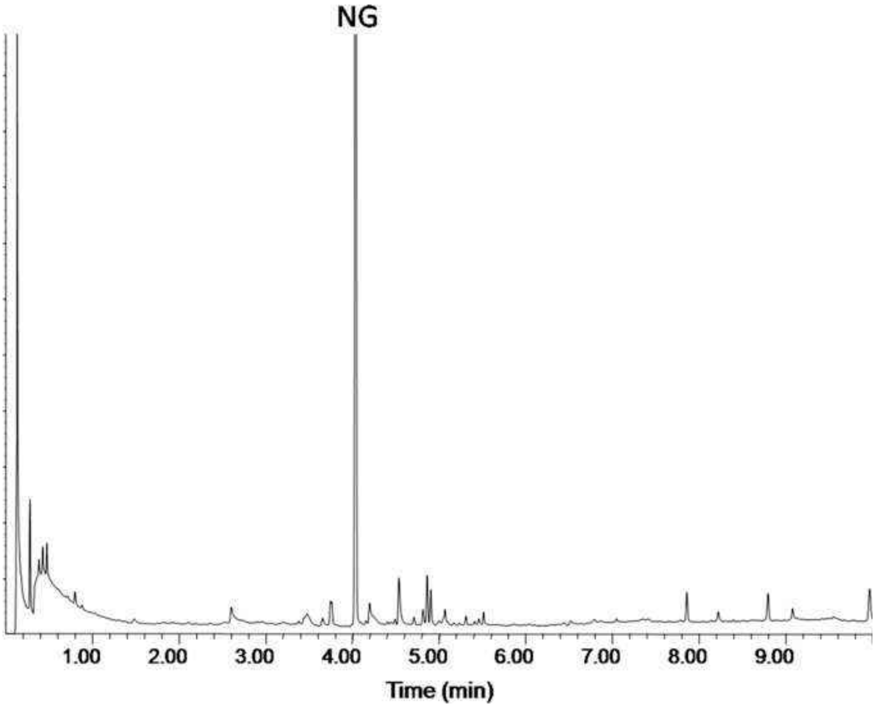


Fig. 8.13 GC-ECD chromatogram for Item 1

ion chromatograms (EICs) for identified analytes common to smokeless powders are displayed in Fig. 8.14.

No inorganic analytes of interest were detected in the water extracts.

Interpretation of Results and Reporting

While nitroglycerin by itself may have non-explosive sources, the presence of the other explosive-related compounds allows for more definitive conclusions. Examples of possible wording for reporting the results would be as follows:

> Nitroglycerin, ethyl centralite, diphenylamine and dinitrotoluene were identified on Items 1 and 2. These components can be found in some smokeless powder formulations. Smokeless powders are low explosive products used as ammunition propellants.
>
> Components of double-base smokeless powder were identified on Items 1 and 2.

8.7.2 Case Study 2 (Post-Blast Analysis for Inorganic Residues)

Scenario

An explosion occurred from an exploding target product placed in an appliance and initiated by the impact of a projectile from a firearm. The appliance parts were collected for submission to the laboratory for post-blast analysis (Figs. 8.15 and 8.16).

Analytical Results

Upon visual examination, translucent white crystals were observed on the inner panels. The residue was collected by scraping and analyzed by SEM-EDS and XRD. The XRD of the scraped residue exhibited preferred orientation (Fig. 8.17; see Chap. 1). Therefore, the scraped residue was further processed using water dissolution and filtration. The soluble portion was dried, and the recrystallized residue was analyzed by SEM-EDS and XRD (Fig. 8.18).

Interpretation of Results and Reporting

The data provided a clear identification of ammonium nitrate crystals which may be reported as in the following examples:

> Ammonium nitrate residue was present.
>
> Ammonium nitrate was identified on the item examined. Ammonium nitrate is a component of some exploding target formulations.

As ammonium nitrate is present in explosives (e.g., ANFO) and commercial products (e.g., fertilizer), examples of each may be reported as well. The decision to include usage examples may depend upon the circumstances of the case as well as the analytical results.

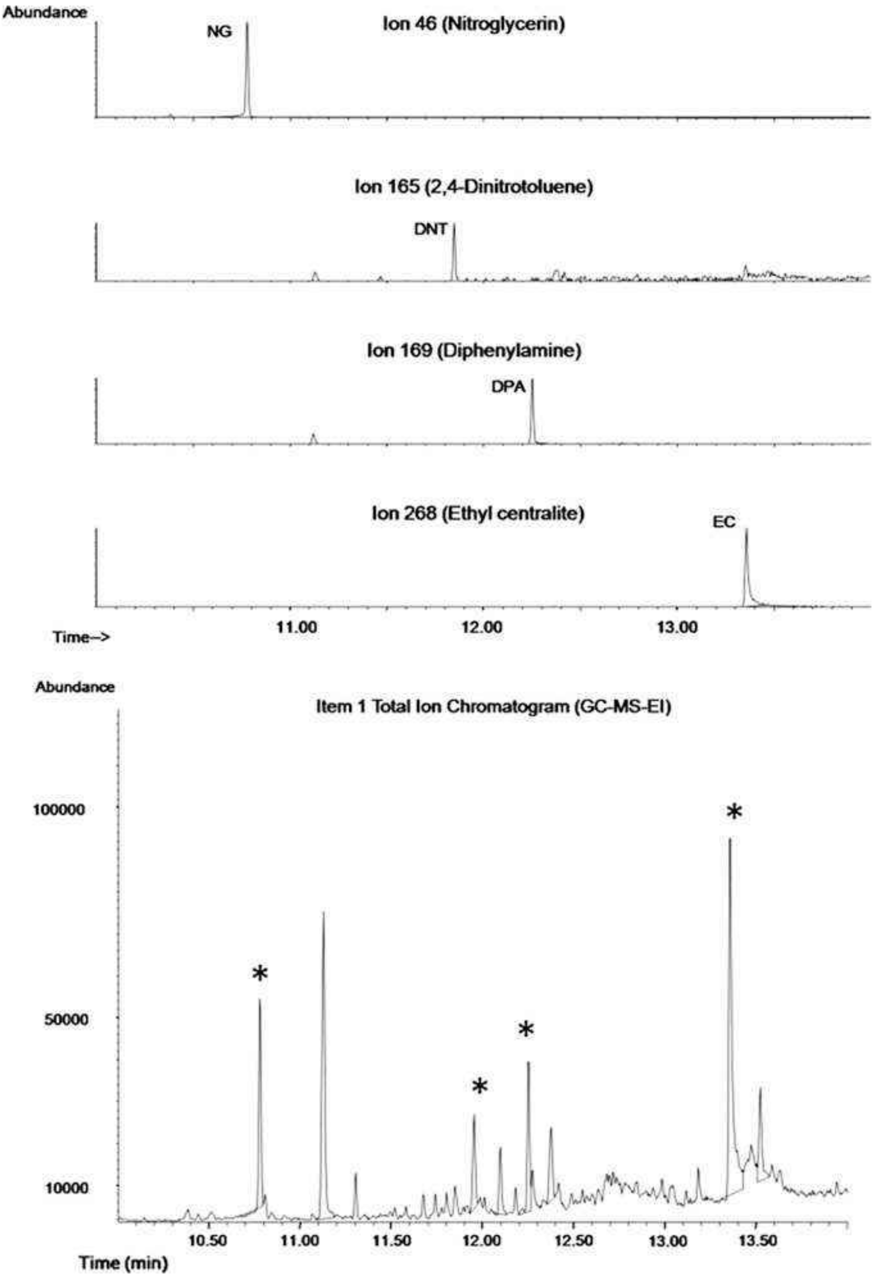


Fig. 8.14 GC-MS-EI total ion chromatogram (bottom) and extracted ion chromatograms (top) for Item 1: NG (m/z 46), dinitrotoluene (m/z 165), diphenylamine (m/z 169), ethyl centralite (m/z 268)

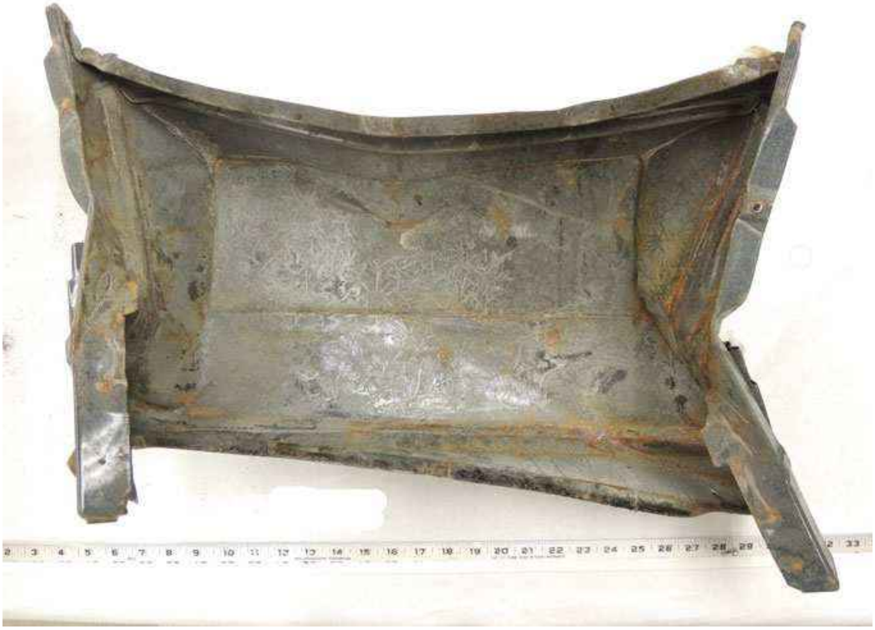


Fig. 8.15 Crystalline material visible on an appliance part

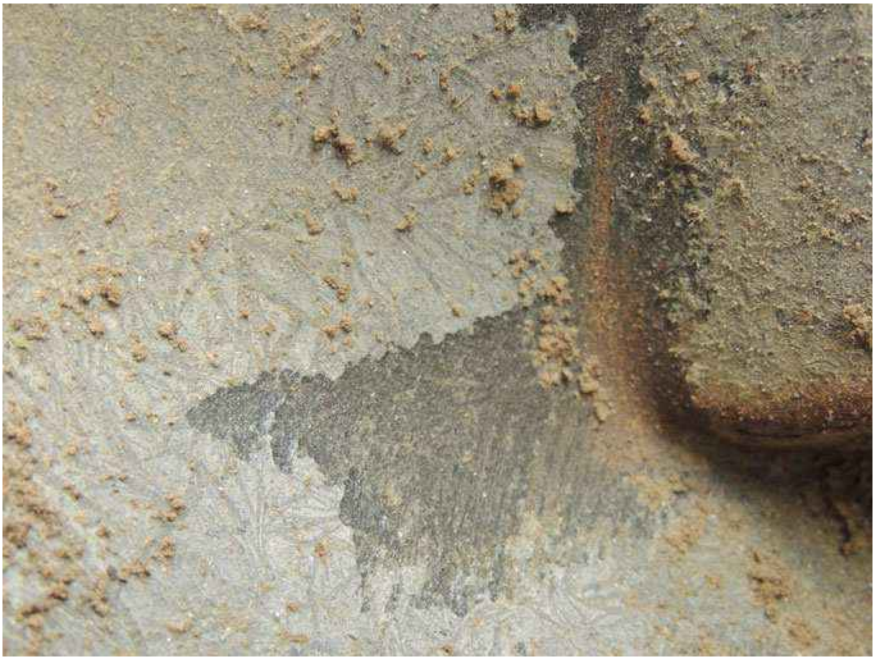


Fig. 8.16 Crystalline material scraped from an appliance part

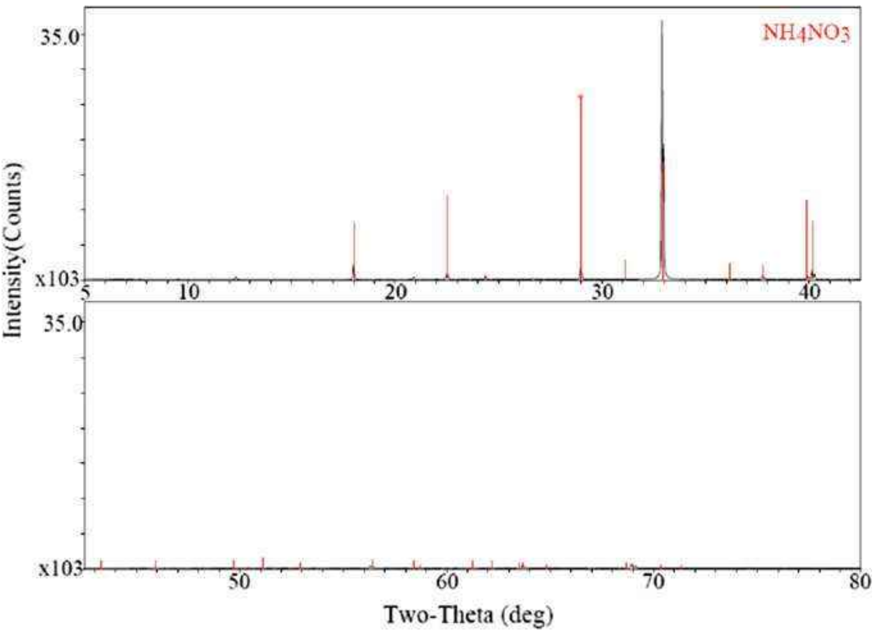


Fig. 8.17 XRD of scraped residue

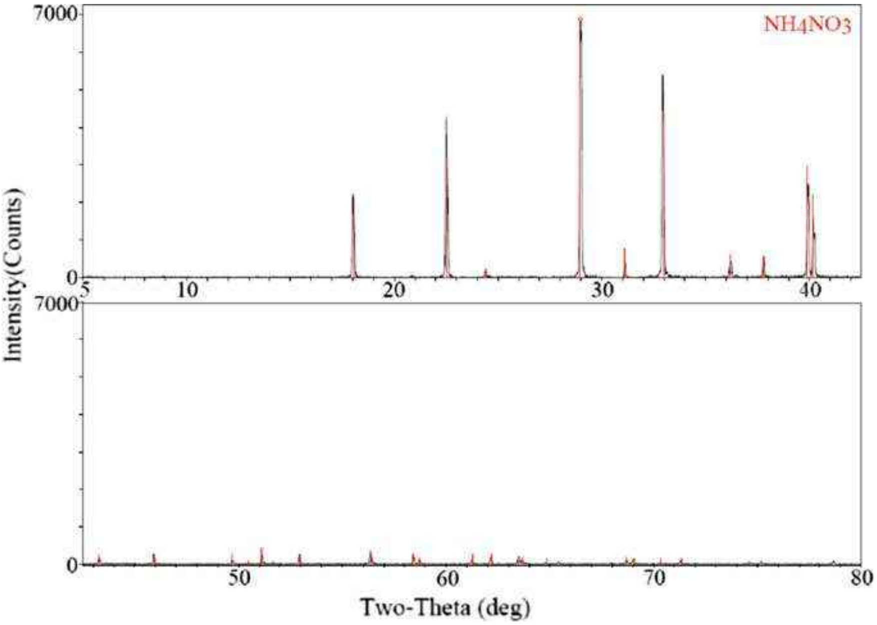


Fig. 8.18 XRD of scraped residue after clean-up procedure

8.7.3 Case Study 3 (Post-Blast Analysis for Inorganic and Organic Residues)

Scenario

A suspected pipe bomb was recovered and functioned while bomb technicians were attempting to render the device safe. The pipe, end caps (Fig. 8.19), and source of initiation were collected and submitted to the laboratory for processing.

Analytical Results

Residues were observed during the visual examination. A small amount was collected and analyzed by FTIR, but the data were inconclusive. The residues were further analyzed by SEM-EDS (Fig. 8.20) and XRD. The data suggested a black powder substitute such as Pyrodex® and Triple Seven®. Due to the chlorine and potassium chloride indicated, the residues were dissolved and analyzed by IC-MS and HPLC.

The pipe and end caps were rinsed with dichloromethane in order to screen for organic explosives. The extract was analyzed by GC-MS and LC-QTOF, which yielded the identification of 2,4-dinitrotoluene and nitroglycerin, components found in smokeless powder.

Interpretation of Results and Reporting

The analytical data in Table 8.5 would be interpreted collectively to determine the inorganic explosive while considering non-explosive contributions. For example, the elements Zn and Fe in the SEM-EDS data were likely from the galvanized pipe (see Chap. 9 for further discussion on pipes). The results from the inorganic and organic analyses would both be reported with the following as an example of suitable wording:

> Post-combustion residues chemically consistent with Pyrodex®were identified. Pyrodex®is a black powder substitute manufactured by Hodgdon Powder Company. Nitroglycerin and 2,4-dinitrotoluene (DNT), chemical components found in smokeless powder, were identified in an extract of the pipe nipple and end caps.

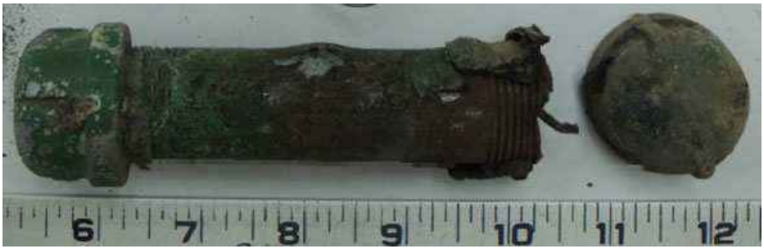


Fig. 8.19 Pipe and end caps

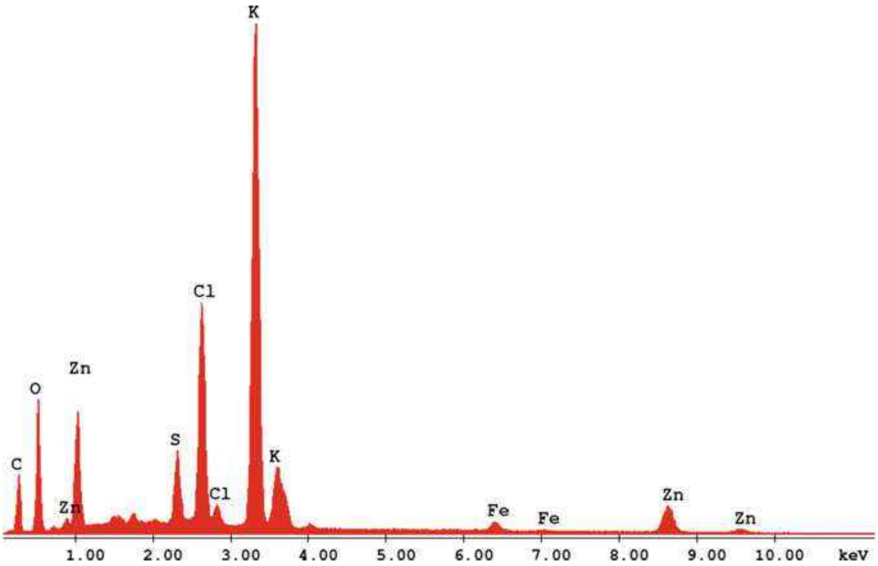


Fig. 8.20 SEM-EDS of collected residues. Zn and Fe likely contributions from the galvanized pipe and/or galvanized cast iron end caps

Table 8.5 Results from the analysis of inorganic residues

SEM-EDS	K, Cl, O, Zn, S, C, Fe
FTIR	Inconclusive
XRD	SiO_2, K_2SO_4, KCl (weak)
IC-MS	Cl^-, NO_2^- (weak), SO_4^{2-}, NO_3^-, ClO_3^-, Benzoate, $S_2O_3^{2-}$, SCN^-
HPLC	Benzoic acid, Cyanoguanidine

8.8 Questions

1. What practices should be taken at the crime scene to minimize and monitor the potential for contamination of explosives?
2. What instruments are commonly used in both intact and post-blast analysis?
3. What is the importance of including method blanks and control samples in analysis of extractions?
4. What is an example of a nitroaromatic explosive?
5. What explosive is indicated by the following data: K_2SO_4 by XRD; O, S and K by SEM-EDS; and NO_2^-, SO_4^{2-}, NO_3^-, $S_2O_3^{2-}$ and $SCN^-$by IC-MS?
6. What are two examples of organic solvent employed in the extraction for organic explosives?

7. If no residues are observed after drying down a water extract for inorganic explosives, what is a possible next step?
8. What is a principle challenge for the interpretation and reporting of post-blast analytical results?

References

1. Song-im N, Benson S, Lennard C (2012) Evaluation of different sampling media for their potential use as a combined swab for the collection of both organic and inorganic explosive residues. Forensic Sci Int 222:102–110
2. Crowson A, Hiley R, Todd C (2001) Quality assurance testing of an explosive trace analysis laboratory. J Forensic Sci 46:53–56
3. Crowson A, Doyle S, Todd S et al (2007) Quality assurance testing of an explosives trace analysis laboratory—further improvements. J Forensic Sci 52:830–837
4. Thompson R, Fetterolf D, Miller M, Mothershead R II (1999) Aqueous recovery from cotton swabs of organic explosives residues followed by solid phase extraction. J Forensic Sci 44:795–804
5. Warren D, Hiley R, Phillips S et al (1999) Novel technique for the combined recovery, extraction and clean-up of forensic organic and inorganic trace explosives samples. Sci & Justice 39:11–18
6. DeTata D, Collins P, McKinley A (2013) A comparison of solvent extract cleanup procedures in the analysis of organic explosives. J Forensic Sci 58:500–507
7. Thomas J, Donnelly C, Waddell R et al (2018) Development and validation of a solid phase extraction cleanup procedure for the recovery of trace levels of nitro-organic explosives in soil. Forensic Sci Int 284:65–77
8. Barshick S, Griest W (1998) Trace analysis of explosives in seawater using solid-phase microextraction and gas chromatography/ion trap mass spectrometry. Anal Chem 70:3015–3020
9. Kirkbride K, Klass G, Pigou P (1998) Application of solid-phase microextraction to the recovery of organic explosives. J Forensic Sci 43:76–81
10. Furton K, Wu L, Almirall J (2000) Optimization of solid-phase microextraction (SPME) for the recovery of explosives from aqueous and post-explosion debris followed by gas and liquid chromatographic analysis. J Forensic Sci 45:857–864
11. Muller D, Levy A, Shelef R et al (2004) Improved method for the detection of TATP after explosion. J Foren Sci 49:935–938
12. Fetterolf D, Clark T (1993) Detection of trace explosive evidence by ion mobility spectrometry. J Forensic Sci 38:28–39
13. Oxley J, Smith J, Kisrshenbaum L et al (2008) Detection of explosives in hair using ion mobility spectrometry. J Forensic Sci 53:690–693
14. Cook G, LaPuma P, Hook G et al (2010) Using gas chromatography with ion mobility spectrometry to resolve explosive compounds in the presence of interferents. J Forensic Sci 55:1582–1591
15. Xu X, van de Craats A, Kok E et al (2004) Trace analysis of peroxide explosives by high performance liquid chromatography-atmospheric pressure chemical ionization-tandem mass spectrometry (HPLC-APCI-MS/MS) for forensic applications. J Forensic Sci 49:1230–1236
16. Xu X, Koeberg M, Kuijpers C et al (2014) Development and validation of highly selective screening and confirmatory methods for the qualitative forensic analysis of organic explosive compounds with high performance liquid chromatography coupled with (photodiode array

and) LTQ ion trap/Orbitrap mass spectrometric detections (HPLC-(PDA)-LTQOrbitrap). Sci and Justice 54:3–21

17. Zhao M, Zhang S, Yang C et al (2008) Desorption electrospray tandem MS (DESI-MSMS) analysis of methyl centralite and ethyl centralite as gunshot residues on skin and other surfaces. J Forensic Sci 53:807–811
18. Nilles J, Connell T, Stokes S, Durst H (2010) Explosives detection using direct analysis in real time (DART) mass spectrometry. Propellants, Explos, Pyrotech 35:451–466
19. Beveridge A (ed) (1998) Forensic Investigation of Explosions. CRC Press, Boca Raton, FL
20. TWGFEX Laboratory Explosion Group Standards & Protocols Committee (2007) Recommended guidelines for forensic identification of post-blast explosive residues. In: TWGFEX Reference Library. http://www.swgfex.com/publications. Accessed 1 Aug 2018
21. Budavari S, O'Neil M, Smith A, Heckelman P, and Kinneary J (eds) (1996) The Merck Index
22. Goodpaster J, Keto R (2004) Identification of ascorbic acid and its degradation products in black powder substitutes. J Forensic Sci 49:523–528
23. Lang GH, Boyle K (2009) The analysis of black powder substitutes containing ascorbic acid by ion chromatography/mass spectrometry. J Forensic Sci 54:1315–1322
24. Bottegal M, Lang L, Miller M, McCord B (2010) Analysis of ascorbic acid based black powder substitutes by high-performance liquid chromatography/electrospray ionization quadrupole time-of-flight mass spectrometry. Rapid Commun Mass Spectrum 24:1377–1386
25. Hargadon K, McCord B (1992) Explosive residue analysis by capillary electrophoresis and ion chromatography. J Chromatogr 602:241–247
26. McCord B, Hargadon K, Hall K, Burmeister S (1994) Forensic analysis of explosives using ion chromatographic methods. Anal Chim Acta 288:43–56
27. Crowson C, Cullum H, Hiley R, Lowe A (1996) A survey of high explosives traces in public places. J Forensic Sci 41:980–989
28. Cullum H, McGavigan C, Uttley C, Stroud M, Warren D (2004) A second survey of high explosives traces in public places. J Forensic Sci 49:684
29. Lahoda K, Collin O, Mathis J et al (2008) A survey of background levels of explosives and related compounds in the environment. J Forensic Sci 53:802–806
30. Walker C, Cullum H, Hiley R (2001) An environmental survey relating to improvised and emulsion/gel explosives. J Forensic Sci 46:254–267
31. Bender E (1989) The analysis of dicyandiamide and sodium benzoate in Pyrodex by HPLC. Crime Laboratory Digest 16:76–77
32. Srinivasan A, Viraraghavan T (2009) Perchlorate: health effects and technologies for its removal from water sources. Int J Environ Res Public Health 6:1418–1442

Brittany Crane Calhoun is a Forensic Chemist in the Bureau of Alcohol, Tobacco, Firearms and Explosives. She specializes in explosives and trace analysis. She also supports explosive canine training and delivers training on homemade explosives.

Robert Mothershead is a Forensic Chemist in the Federal Bureau of Investigation. He specializes in fire debris and explosive analysis, and has almost twenty years of experience in post-blast evidence collection and analysis. He has also co-authored peer-reviewed journal articles on trace explosive analysis.

Chapter 9
Explosive Device Componentry and Evaluation

Kirk Yeager and John Jermain

Learning Objectives

- Recognize what is meant by an improvised explosive device (IED) and the types of evidence collected in bombing investigations.
- Recognize the types of components typically utilized to produce explosive or incendiary devices.
- Understand the process utilized in the forensic exploitation of explosive devices, and the conclusions reached by examiners through these examinations.

9.1 Introduction

From the time alchemists discovered explosive compounds and mixtures, they have been used to produce contrivances that explode. Such devices came to be known as "bombs." Bombs outside their application by military forces went by many names over the centuries ranging from the historically poetic "Infernal Machine" to the current day "IED." Regardless of what name they went by, they shared a common purpose. Even though bombers may on occasion turn to military ordnance to commit their crimes, this chapter will focus solely on the analysis of improvised explosive devices.

Current military training manuals define **improvised explosive device (IED)** as "A device placed or fabricated in an improvised manner incorporating destructive, lethal, noxious, pyrotechnic, or incendiary chemicals and designed to destroy,

---

K. Yeager (✉)
Federal Bureau of Investigation, Quantico, VA, USA

J. Jermain
Bureau of Alcohol, Tobacco, Firearms and Explosives, Huntsville, AL, USA

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_9

incapacitate, harass, or distract. It may incorporate military stores, but is normally devised from nonmilitary components [1].” In all manifestations, these devices possess the shared attribute that they are designed to damage, hurt, or kill.

These devices have also been defined for purposes of the law. In the legal world, a bomb may often be referred to as a “**destructive device.**” The definition of what constitutes a destructive device can vary from jurisdiction to jurisdiction. For example, this is a section from the definition of a destructive device used at the federal level:

> Any explosive, incendiary, or poison gas—(i) bomb, (ii) grenade, (iii) rocket having a propellant charge of more than four ounces, (iv) missile having an explosive or incendiary charge of more than one-quarter ounce, (v) mine, or (vi) device similar to any of the devices described in the preceding clauses [2].

This chapter will cover the components typically used to produce an IED, as opposed to the actual explosive/explosive residues discussed in Chaps. 7 and 8. Although the forensic examinations applied in analyses of IEDs will be presented, discussions of legal interpretations are beyond the scope of this book.

9.2 Overview of IED Construction

To fully understand the vast array of materials that can be used to produce an IED, a higher-level overview of their construction is required. Every IED consists of two basic pieces: an explosive charge and some means of initiating the explosive. Obviously, an IED would be difficult to produce without incorporation of a material capable of exploding. The mechanism utilized to initiate the explosive is referred to as the **fuzing system** or **initiating system**.

Fuzing systems are categorized as one of two types: electric or non-electric. The characteristic which differentiates the two is whether or not electricity is required in the operation of the system’s mechanisms. An electric fuzing system requires an electric current for it to function. No such current is required in a non-electric fuzing system.

9.2.1 Non-electric Fuzing Systems

Non-electric fuzing systems tend to be the most rudimentary. All function by introducing heat in some form into the explosive. Heat is imparted into the explosive through either mechanical or chemical means. In mechanical systems, impact is often used to introduce energy. The striking of a gun’s firing pin against a cartridge’s primer is an example of this type of mechanical energy transfer into heat energy. This same energy transfer is also seen utilized in the spring-loaded strikers used to initiate hand grenades.

In non-electric systems utilizing chemistry, chemical reactions are responsible for introducing the heat needed to initiate the IED. The classic chemical system is a burning length of time fuse (not to be confused with fuze; see inset). Time fuse consists of the explosive black powder encased in a weather-resistant covering designed to transmit a chemical burning reaction at a predictable rate.

Fuse - a length of material along which a small flame moves to initiate an explosive.

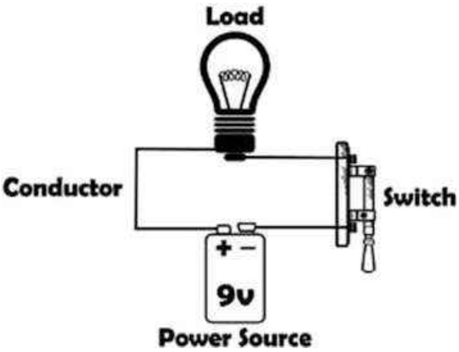
Fuze - a mechanism used to initiate an IED.

Another method of initiation uses chemical reactions that create spontaneous ignitions. These **hypergolic reactions**, which will be discussed further in Chap. 10, can result when two highly reactive chemicals are brought in contact with each other. If the proper chemicals are selected, they can react violently enough to produce combustion and flame. Hypergolic reactions have been used for decades to initiate IEDs. On Christmas Day 2009, while aboard a transatlantic flight, Umar Farouk Abdulmutallab pushed the plunger of a syringe containing just such a combination of chemicals. Within seconds, they combusted and set off part of the fuzing system of an IED secreted in his underwear. In this case, a failure in other parts of the fuzing system resulted in its failure to initiate his main explosive charge.

9.2.2 Electric Fuzing Systems

Electric fuzing systems are more diverse than non-electrics as a much broader array of components can be applied to their production. An electric fuzing system, such as the one shown in Fig. 9.1, contains four main parts; a “load,” a power source, a

Fig. 9.1 Electric fuzing system [3]



conductor, and at least one switch. In this application, "**load**" is the technical term for the component in the system which supplies the energy to initiate the IED. Loads will be discussed in much greater detail in the componentry section.

Electric fuzing systems rely on electricity to generate the energy required to initiate an IED. For them to function, there must be a source of electrical current. In most cases, the **power source** for an IED is a battery of some sort. Batteries provide mobility to IEDs, and mobility introduces flexibility in placement. Using household current is a possibility, but it is rarely applied as a power source in electric systems because it limits the mobility of the IED.

To get current from the power source to the load, a **conductor** is required. Most electric systems use copper wire to serve as the conductor. In more sophisticated devices, the conductor can also incorporate circuit boards with electronic components.

A critical part of the electric fuzing system is the switch. The switch is what allows current to flow from the power source through the conductor into the load at a time and place theoretically selected by the bomber. Two general types of switches exist: an arming switch ("safe arm") and a firing switch ("trigger"). Every IED that uses an electric fusing system requires a **firing switch** for it to function. An arming switch can be present to add an increased degree of safety for the perpetrator. Figure 9.2 shows a simulation of an IED. Two switches are seen in the IED. The **arming switch** at the top must be activated before the tripwire will be able to function the mousetrap firing switch. The mousetrap switch consists of a screw inserted into the wooden base of the mousetrap. A small piece of wood attached to a piece of fishing line is placed between the screw and the metal swing arm of the trap. When the wood is pulled out by the fishing line, the swing arm

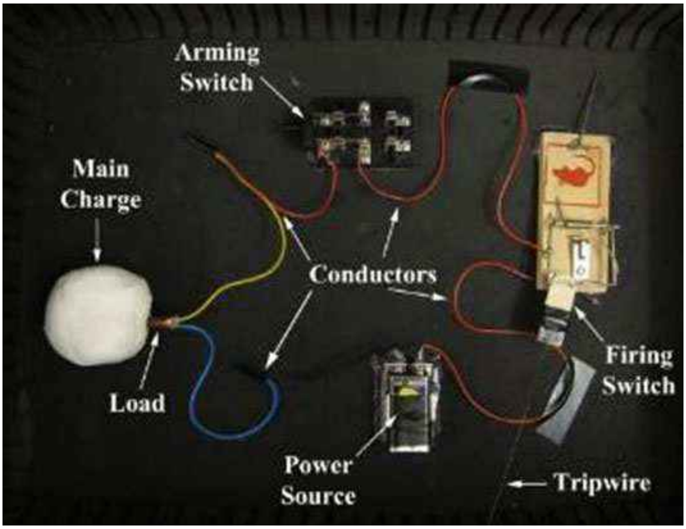


Fig. 9.2 IED components assembled

touches the screw, electrical contact is made, and the device functions. A 9 V battery serves as a power source. The load is a detonator seen inserted into the main charge explosive. The flow of electricity from the battery to the detonator can be traced by following the wiring used as the conductor. There are a wide variety of switches that can be used in an IED. Numerous examples will be discussed in the componentry section of this chapter.

9.3 Forensic Examinations of IEDs

Explosive device examinations are carried out by a broad array of laboratories worldwide. This type of analysis is not limited to law enforcement, as it is applicable to the analysis of IEDs recovered in war zones as well as those utilized in criminal acts. Regardless of the end use of an IED, the forensic science dedicated solely to the device construction and analyses brought to bear in this discipline will be focused to two areas: identification of device components and determination of device functionality. Examiners strive to understand what items were used to construct an IED, and how the components utilized to produce it worked in concert to make it explode.

Examinations of device components consist of identifying the constituent parts used in construction and exploiting them for forensic information of value. A more detailed description of the types of components typically found in IEDs will be presented in Sect. 9.4. When examining components, forensic scientists conduct a wide variety of analyses of their physical attributes which may involve:

(1) *gauging and analyzing wire;*
(2) *analyzing physical and chemical make-up of wire/connector insulation;*
(3) *measuring/determining pipe or end cap dimensions;*
(4) *measuring and analyzing enhancements added to the device (nails, screws, shot, BBs,* etc.*) and/or fragments from an exploded device's housing and fuzing system (pipe, grenade,* etc.*).*

Examiners will often compare device components to exemplars, if available, in order to identify components. An example of this process will be provided in Sect. 9.3.3.

The goal of the explosive device "functionality" examination is to determine both the characteristics of how a device, or its constituent parts, was arranged and the manner in which the assembled components could work in concert to create an IED. Each organization may divide responsibilities for such examinations in a different fashion (as previously discussed in Chap. 7). However, anyone analyzing a device's functionality must follow a similar set of logical steps.

Device functionality examinations focus on the fuzing system and componentry used in the IED itself. The methodology applied by forensic examiners who focus on explosive devices can be broken down into five steps:

1. *Segregation—items present in evidence are reviewed to determine those both relevant and not relevant to the IED, with those judged as relevant separated for further examination.*
2. *Recognition—submitted specimens are examined with the intent of finding items which could potentially function in the capacity of components of an IED.*
3. *Identification—determine what types of components are present in submitted specimens and their potential sources.*
4. *Function Determination—attempt to ascertain items' roles in the device being examined.*
5. *Comparison—compare device componentry to items of evidence seized from a suspect, or comparisons of separate devices, such as those used in serial bombings.*

Depending on the nature of the submitted specimens, it may not be possible to take every item of evidence through these five steps. They are provided only as an outline of the approach taken by an examiner while conducting the analysis of evidence. They may be conducted in parallel or in any logical sequence depending on the nature of the evidence. Different organizations may use different nomenclature when referring to these steps, but all explosive device examinations follow the logic outlined. The FBI forensic analysis of the Collar Bomb illustrates these steps.

On Thursday, August 28, 2003, at approximately 2:30 PM Brian Wells walked into the PNC Bank in Erie, PA with a homemade shotgun in one hand and a ticking time bomb strapped around his neck. Within an hour the IED would explode, killing Wells instantaneously and launching a 7-year investigation. The Collar Bomb employed many unique components and required an extensive analysis to discern how it was assembled and functioned.

9.3.1 Segregation

IEDs can be constructed from numerous commercially available or homemade items. Often items submitted as evidence to the laboratory as part of a bombing investigation were not part of the IED and may consist of background debris from the bombing scene. The segregation process involves the separation of items of potential forensic value for further examinations by either bombing specialists or forensic examiners from relevant disciplines.

An example of segregation is provided in Fig. 9.3. The picture shows the contents of one bag of evidence sent in during the Collar Bomb investigation. When an IED explodes, it can severely damage the container used to house it and the components of its fuzing system. Often, this makes it very challenging to determine what evidence submitted was actually part of the IED, and what items might have been "background materials," or items present on scene damaged by the explosion. Often careful examination of the surrounding area will have to be conducted to

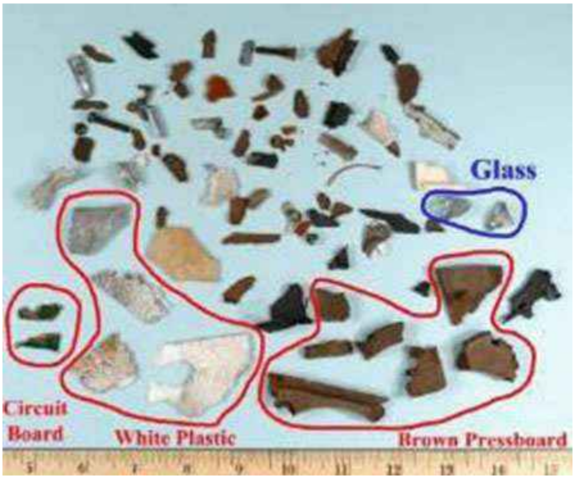


Fig. 9.3 Segregation of evidence

allow true segregation of items relevant to an IED. For example, in a car bomb it may be necessary to look at the wiring of the vehicle itself to segregate out damaged vehicle wiring from wiring used to construct the IED.

Items initially segregated from the Collar Bomb submission for further analysis (circled in Fig. 9.3) consisted of circuit board fragments (lower left), thin white plastic fragments, and thick brown pressboard fragments (bottom). Pieces of broken glass (middle right) were segregated out, judged to have not come from the device.

9.3.2 *Recognition*

The recognition step involves a visual examination of the segregated items in an attempt to assign general attributes, or class characteristics, to items that could potentially function as parts of the fuzing system, concealment container, or added enhancements.

During the early stages of the Collar Bomb analysis, various items were quickly recognized. Depicted in Fig. 9.4 are multiple sections of a circuit board (upper left), small shotgun pellets (below the circuit board fragments), and a length of red wiring. All of these were recognized for the role they could have played in an IED. The brown pressboard (seen lower left) was segregated out due to the explosive damage it exhibited and the lack of any such material native to the scene of the explosion. During the early stages of the analysis, its function in the device was not recognized, nor was it possible to identify the material of which it was comprised.

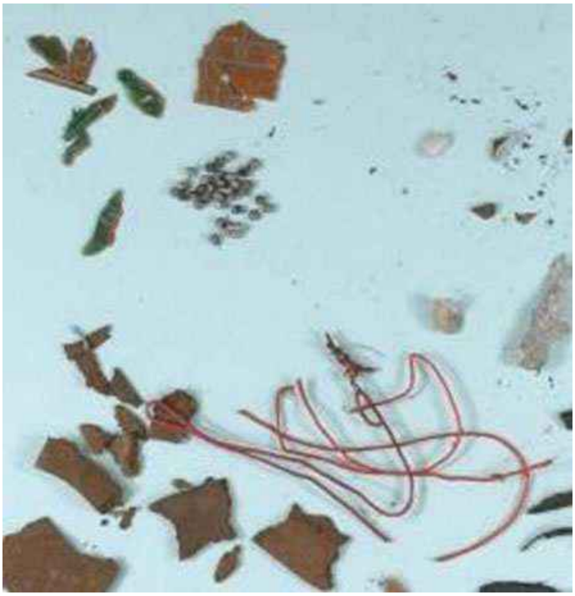


Fig. 9.4 Recognition of device components

9.3.3 Identification

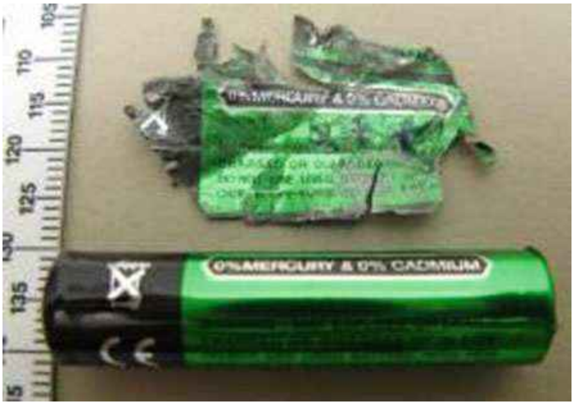
The concept of identification utilized in device examinations is somewhat different from that applied in other forensic disciplines in that the identification of a particular component does not designate the determination of a component's origin to the exclusion of all other possible sources. That is, the use of the term does not imply that the item's origin is linked with a specific individual. The term identification is used in device examinations to designate the types of IED components that are present in the evidence and their potential manufacturing sources.

Pictured in Fig. 9.5 is an identification eventually made in the Collar Bomb case. The fragment of green label in the top portion of the picture was recognized as the thin metal skin from a battery. Enough unique markings were left on the skin to eventually lead to identification as an AA battery from a particular manufacturer. In addition, other pieces of evidence analyzed revealed that fragments of an electronic timer were contained in the evidence. When the timer type and model were identified, it was discovered that this timer was sold with the same make and model of battery previously identified in the evidence.

9.3.4 Function Determination

Once all of the components have been identified to their fullest extent, attempts to determine their role in the functioning of the IED are made. It is emphasized in this

Fig. 9.5 Identification of battery fragment



step that the destruction created by the forces from the explosion of an IED may render a definitive determination of how it functioned impossible. The forensic examiner may be limited to only logical conjecture on the role of the components in the functioning of the IED, as well as exactly how the IED might have been constructed and functioned as a whole. Education, training, and experience must be used to deduce the most logical functioning of the device. It is also essential to recognize on occasion that more than one hypothesis to a device's functioning might be possible.

Pictured in Fig. 9.6 is a long metal bar segregated out of the evidence submitted in the Collar Bomb case. It was obvious this had to be part of the IED, as it was custom made and heavily damaged. The apparent custom fabrication negated the need to try to identify any commercial source for the item.

Function determination for this item was particularly challenging. The battery depicted earlier was a potential power source for the IED. It took months before the bar's use could be ascertained. Pictured in Fig. 9.7 is the component put back in place in the reconstructed IED. It is worth noting that the thick brown pressboard material seen earlier was eventually identified as Masonite, a type of engineered

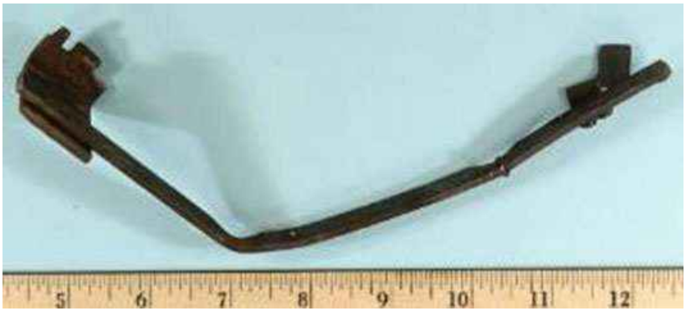


Fig. 9.6 Long metal bar submitted to laboratory

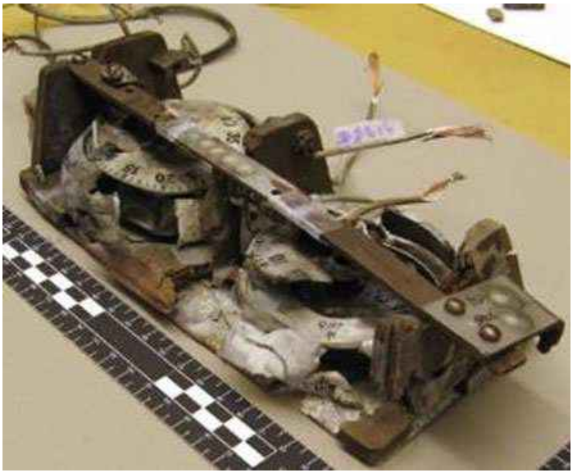


Fig. 9.7 Metal bar put in place in reconstructed device

wood product seen in construction. The function of this Masonite was eventually determined to be part of a structure built to hold two kitchen timers in place. The metal bar can be seen sitting on top of grooves cut into the Masonite timer housing.

It was determined that the metal bar served as a way to deactivate the IED if the proper sequence of events was carried out. This determination was made by reconstructing the IED from the fragments and ascertaining how the metal bar fit into various other IED components. The bar was modified with the addition of a thick layer of glue on one end to allow it to block another metal bar attached to one of the kitchen timers from contacting a screw drilled into that timer's face. Thus, the timer acted as a switch and the metal bar as a way of blocking that switch from closing.

9.3.5 Comparison

There are two general types of comparison examinations that occur in the discipline of explosive devices' examinations: IED/known origin comparisons (between the components of an IED and items of known origin), and inter-device comparisons (between the components of multiple IEDs). In both examinations, comparisons are made between the observable, physical characteristics of various items to determine if they are similar. Simple observable characteristics such as shapes, colors, or markings on the components may be compared. The examinations may also involve the comparison of measured physical characteristics such as length, diameter, width, weight, and thickness of the components. In addition, chemical analysis may be utilized for some components in an attempt to further discriminate items that are believed to be similar.

To show an example of both types of comparisons, the Unabomber case will be used. In 1978, Theodore Kaczynski produced his first, primitive homemade IED which exploded at a Chicago university. Over the next 17 years, he mailed or hand-delivered a series of increasingly sophisticated IEDs that killed three Americans and injured 24 more. In 1979, an FBI-led task force was formed to investigate the "UNABOM" case, code-named for the UNiversity and Airline BOMbing targets involved. The task force would grow to more than 150 full-time investigators, examiners, and others. In search of clues, the team made every possible forensic examination of recovered IED components and studied the lives of victims in minute detail. These efforts proved of little use in identifying the bomber, who took pains to leave no forensic evidence, building his IEDs essentially from "scrap" materials available almost anywhere. Victims, investigators later learned, were chosen randomly from library research.

Ted Kaczynski deployed 16 IEDs during his serial bombing campaign. Early on, it became very important to determine if a device that exploded was his handiwork, requiring inter-device comparisons. When Kaczynski's cabin was searched, a fully completed IED was found under his bed, ready to be mailed off to his next victim. This yielded rich evidence to enable comparisons against previous devices attributed to him.

Seen in Fig. 9.8 are three of Kaczynski's switches from his 13th, 14th, and 15th devices. One way these devices were linked, post-blast, was the presence of this unique homemade switch. When the search warrant was conducted on his cabin, it turned up a fully assembled switch (seen far right). The relationship between this intact switch and the remnants of those utilized in previous devices is obvious. This comparison was utilized as a part of the evidence that linked Kaczynski with the earlier devices.

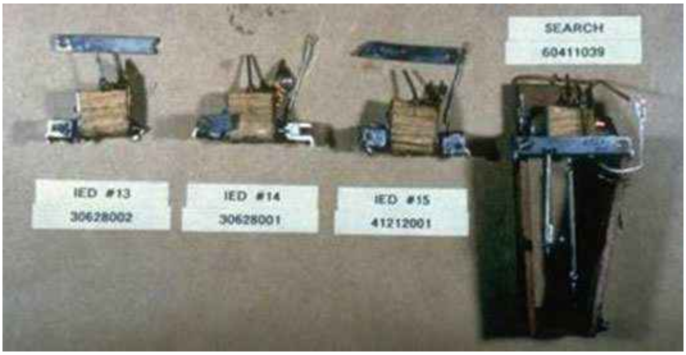


Fig. 9.8 Unabomber switches

9.4 Components of an IED

Components encountered in an IED will vary greatly depending upon the explosives being utilized and the intended target of the bomber. If a low explosive, such as black powder, is the main charge in the device, then some type of confinement to create pressure build-up will be necessary in order to create an explosion, as discussed in Chap. 7. A high explosive, on the other hand, does not require confinement to create an explosion. However, most high explosives employ a more complex fuzing system than a simple length of pyrotechnic fuse. Depending upon the intended target of the bomber and the ability of the bomb maker, the components encountered in an IED may be very simple or quite complex. A victim-operated device will tend to have a complex fuzing system, which may have an arming switch to allow the bomber to transport the explosive device safely, as well as a firing switch to initiate the explosive charge, as seen in Fig. 9.9. The bomber may also add enhancements, such as nails and BBs, to the IED to increase lethality. However, if the IED is intended solely to cause property damage, the fuzing system may simply consist of a length of pyrotechnic fuse.

The five most commonly encountered components of an IED are a switch, a power source, an initiator, a container, and the explosive main charge. The acronym **"SPICE" (Switch, Power source, Initiator, Container, and Explosive)** can be used to help investigators remember these components. First responder training often simplifies this to **PIES (Power Source, Initiator, Explosive, and Switch)**. Depending on the construction of the IED, not all of these components will

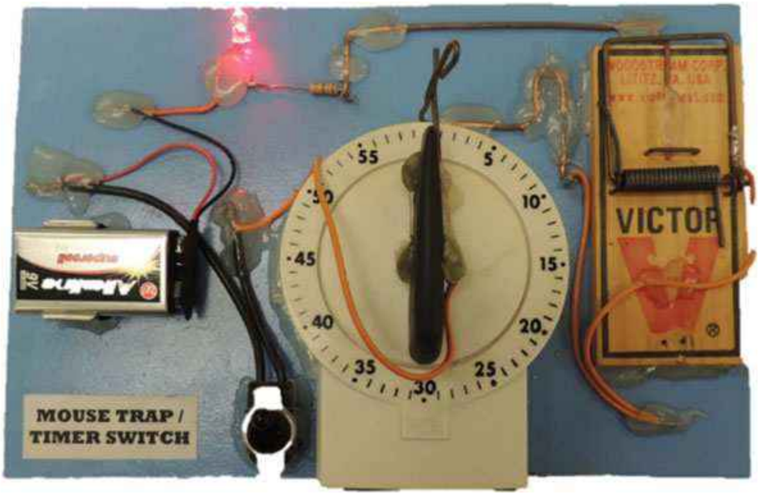


Fig. 9.9 An electric fuzing system consisting of a kitchen timer (arming switch) and a mouse trap (firing switch)

necessarily be encountered. In some cases, additional components, such as enhancements, will be utilized.

9.4.1 Switches

A variety of switches, from commercial to improvised, may be employed to either trigger the explosive device to function or to arm the explosive device to allow the bomber to transport it without it going off prematurely. No matter what type of switch is being used, it will function in one of three ways: **command-operated, time-operated, or victim-operated**. Below is a list of some switch types that can be incorporated into the fuzing system of an IED:

• Anti-disturbance • Photo cell • Radio controlled • Trembler	• Chemical delay • Pressure • Tension-based • Vibration	• Magnetic • Proximity • Timing mechanism

A command-operated switch is activated by the bomber, who has control at the moment of initiation. This type of switch can include a cellular phone, a two-way radio transceiver, a toy remote controller, or a car alarm remote. A time-operated switch is activated at a predetermined time selected by the bomber. This type of switch can include a kitchen timer, an electronic watch, a length of pyrotechnic fuse, or a chemical reaction that can be used to initiate the explosive. A victim-operated switch is activated by the actions of an unknowing individual/victim. This type of switch can include a pressure switch such as a microswitch, a tension switch such as a toggle switch, or a trembler switch such as a mercury switch.

In some instances, an improvised switch can be used in place of a commercially purchased switch. Figure 9.10 shows an improvised victim-operated switch composed of a loop of copper wire and a screw on a spring. Vibrations cause the screw to sway and make contact with the copper loop and thus set off the IED. When analyzing evidence collected from a post-blast scene, the switch will generally survive the explosion, though it may have fragmented into several pieces. If the switch used in the explosive device was commercially manufactured, such as from the internal components from a remote-control car or a microswitch, it may be possible to determine the original manufacturer from markings on the switch.

9.4.2 Initiators

The method used to initiate an IED will differ depending on the explosive charge present. As mentioned in Chap. 7, low explosives, such as black powder, can be

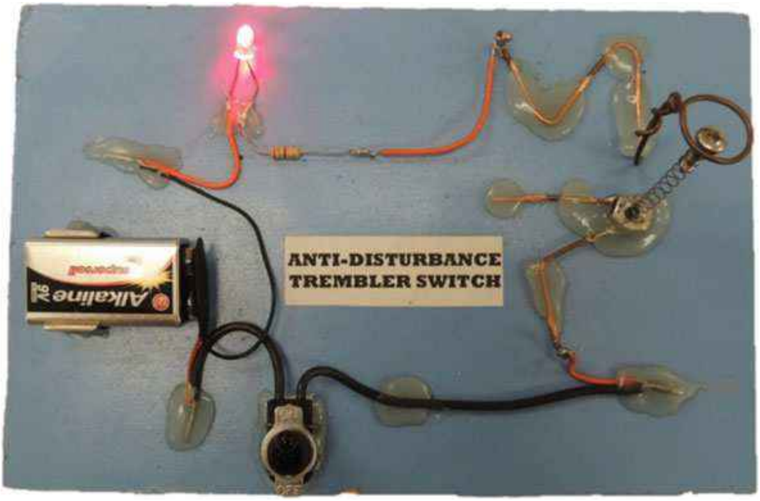


Fig. 9.10 An electric fuzing system consisting of an improvised trembler switch

initiated by heat from an exposed filament or a flame source. Primary explosives, such as lead styphnate and TATP, can also be initiated in a similar manner due to their sensitivity to heat. Primary explosives, unlike low explosives, produce a detonation reaction that releases shock energy when initiated. Secondary high explosives, such as Composition C4 and TNT, as well as blasting agents, such as ANFO, require a large shock to produce a detonation. Typically, the shock energy created by a small quantity (grams) of primary explosive detonating will be required to initiate a secondary explosive. Due to the range of energy input needs, a variety of initiators can be deployed to set off the explosive charge in an IED.

As discussed earlier, initiators can be divided into two categories: electric and non-electric. Electric initiators, as their name implies, need electricity; therefore, a more complex fuzing system is required in order to employ them properly. An **electric match**, for example, consists of two insulated lead wires, which are joined together by a thin bridgewire. The bridgewire is generally coated in a pyrotechnic mixture. When electric current is run through the lead wires, it meets increased resistance at the bridgewire and heats up this thin wire. This heat produces a flame when it reaches the ignition temperature of the pyrotechnic mixture coating the wire. An electric match can be used to initiate low explosives and primary explosives; however, it does not have the energy needed to initiate secondary high explosives or blasting agents. For these less sensitive explosives, a blasting cap (or detonator) is required to create the necessary shock for initiation.

As shown in Fig. 9.11, a blasting cap consists of a cylindrical metal shell containing a sensitive primary explosive, known as the ignition charge, and a secondary explosive, known as the base charge. When the primary explosive is initiated inside the blasting cap by a heat or flame source, it rapidly goes from

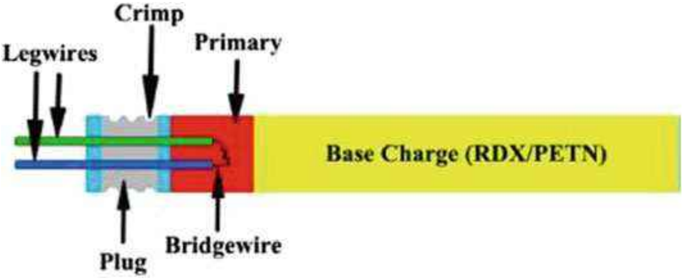


Fig. 9.11 Schematic of electric blasting cap

deflagration to detonation and creates a shock wave that contains enough energy to set off the base charge. The base charge in a detonator will typically contain a small amount of RDX or PETN. The detonating base charge will amplify the energy put out by the primary explosive, rupture the metal casing and, in turn, detonate the main explosive charge. Blasting caps can be initiated electrically (in the same manner as the electric match described earlier) or non-electrically using a length of burning safety/time fuse.

If a blasting cap functioned as part of an explosive device, the post-blast remains can be utilized to determine the manufacturer. Typically, the remains of a blasting cap, if present, will consist of the leg wires, the closure plug where the wires are inserted, and the lower portion of the metal shell. The leg wires of a blasting cap are generally constructed of solid core copper or iron in a variety of sizes (gauges). The wires are insulated with a plastic coating and color-coded to provide product identification. The wires are inserted into a closure plug, which is inserted inside the metal shell. In order to keep the plug from loosening, the manufacturer will squeeze the open end of the metal shell around the plug, which can leave a distinct mark called a “crimp.” By analyzing the color, metal composition, and size of the leg wires; the color and material of the plug; the pattern of the crimp on the shell; and the metal composition of the shell remains, it is possible to link the blasting cap remains to a specific manufacturer.

A commercial model rocket igniter is another example of an electric initiator that has been seen in explosive casework. They can be purchased from a variety of internet sources or from a hobby store that sells rocketry kits. A rocket igniter consists of two non-insulated lead wires which are joined together by a thin bridgewire, which may be coated in a pyrotechnic composition, as in electric matches. By analyzing the pyrotechnic composition as well as the wires for their metal composition and dimensions, it is possible to determine the manufacturer of the rocket igniter.

In some instances, an improvised electric igniter can be used in place of a commercially purchased igniter, as was the case in the Boston Marathon Bombings in 2013, the New Jersey/New York IED attacks in September of 2016, and the attempted bombing of the New York City subway in December of 2017. In all three

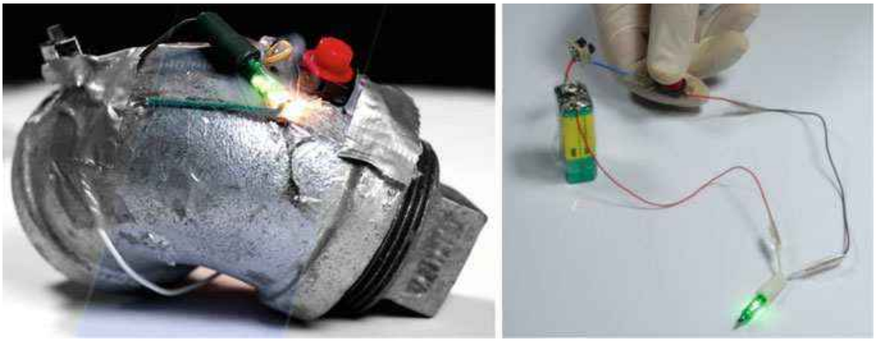


Fig. 9.12 An improvised hand grenade and an electric fuzing system (left). Fuzing system consisting of a Christmas tree light bulb igniter, a 9 V battery, a slide switch (arming switch) and a push-button switch (firing switch) on the right [4]

incidents, the bombers used Christmas tree light bulbs as the initiator for their explosive devices. The use of a Christmas tree light bulb as an improvised electric igniter has also been publicized in a number of articles beginning in summer of 2010 in Inspire Magazine, an online magazine reported to be published by al-Qaeda in the Arabian Peninsula (AQAP) (Fig. 9.12).

Non-electric initiators do not require any form of electricity; therefore, the fuzing system needed for this type of IED is relatively simple. The most prevalent type of non-electric initiator used in an IED is a length of pyrotechnic fuse, also referred to as visco, hobby, or cannon fuses. Pyrotechnic fuse consists of an energetic material, such as black powder, which is typically wrapped in layers of fiber. The outer layer is usually coated in a nitrocellulose lacquer to prevent the fuse from unraveling as well as to preserve the explosive material within. By analyzing the energetic material inside the fuse, as well as dissecting the layers of fiber and counting each strand, a forensic examiner can compare a pyrotechnic fuse from a device to a pyrotechnic fuse found during a search warrant to see if they are similarly constructed.

Other non-electric initiators encountered in explosive devices include quick-match, safety fuse, military time fuse, and, as previously mentioned, hypergolic reactions. Quickmatch is primarily used to initiate the lift charge in pyrotechnic aerial shells. Quickmatch typically consists of strands of fiber coated in finely ground black powder. The strands are placed inside of a paper tube which increases the overall burn rate. Safety fuse, also referred to as time fuse, was prevalent when mining operations used non-electric blasting caps. It has a black powder core and is wrapped in a similar fashion to pyrotechnic fuse; however, it has additional layers such as asphalt, textile threads, and a plastic coating to allow it to be used in damp environments. Safety fuse is still used today in a limited number of applications, such as the initiator for avalanche control devices. The US military has a version of time fuse, M700, which has an olive-drab plastic coating with yellow bands spaced out at different intervals around the outside. This allows for an individual to cut the fuse at a predetermined length, which corresponds to burn delay, without having to take the time to measure the fuse on the battlefield.

9.4.3 Wires

When analyzing a wire used in an explosive device, a forensic examiner may determine the size, metal composition, insulation material, and in some instances, the manufacturer of the wire. This information, as well as other specifications, such as temperature ratings and voltage, can be marked on the insulation material covering the wire. Wire recovered from the explosive devices used in the 2013 Boston Marathon Bombings (shown in Figs. 9.13 and 9.14) could be traced to the original manufacturer since the insulation was marked with the size of the wire, “14 AWG”

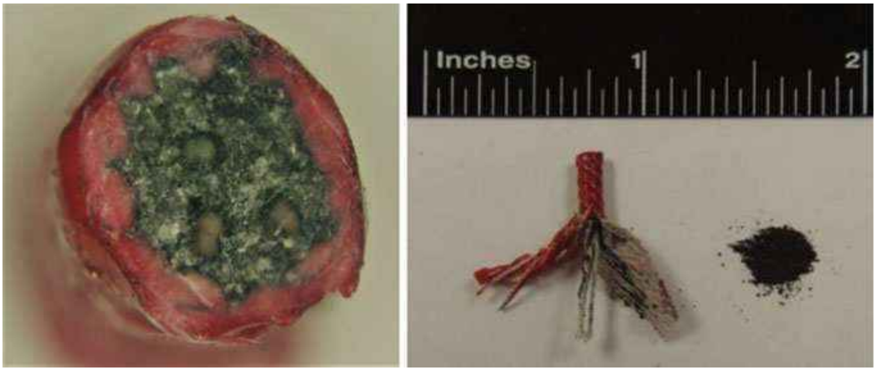


Fig. 9.13 Length of dissected red pyrotechnic fuse. Inner core left and fuse fiber wraps with a black powder core at right

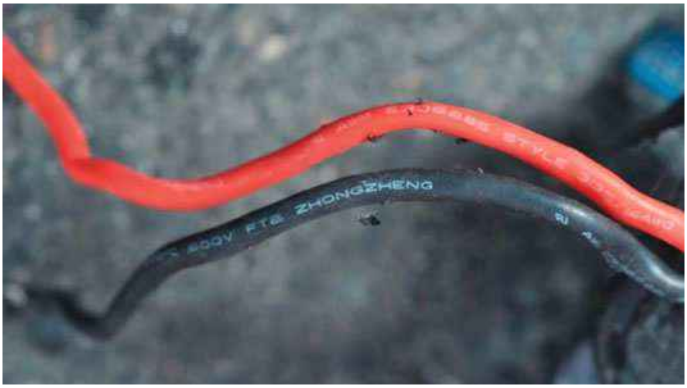


Fig. 9.14 Wires recovered from the Boston Marathon Bombing

(AWG: American Wire Gauge), the type of wire, "STYLE 3135," and the manufacturer of the wire, "ZhongZheng." This information may not be available in some instances; therefore, it is up to the forensic examiner to classify the wire to assist with the investigation.

A wire will either consist of a single metal core or several thinner metal cores bundled together into a cohesive bunch. To determine the size of a solid core wire, the forensic examiner can measure the diameter using a micrometer or digital caliper. Once determined, the diameter is then compared to a wire gauge chart (either commercial or ASTM) to ascertain the size of the wire. For a multi-stranded wire, a few calculations are needed in order to determine the size of the wire. First, the number of strands (n) in the wire must be counted, and second, the diameter of at least one of the strands (d) must be measured. It is best to measure multiple strands and take an average as some variance can exist. If there are visually different sizes of stands present, each type of strand must be measured. Once this information is determined, the diameter of a multi-stranded wire can be calculated using the three equations below.

$$\begin{array}{ll} \mathrm{s} = \left(\pi \times \mathrm{d}^2\right)/4 & s = \{\text{area of a single strand}\} \\ \mathrm{S} = \mathrm{n} \times \mathrm{s} & \mathrm{S} = \{\text{area of a defined number of strands}\} \\ \mathrm{D} = \sqrt{(4\mathrm{S}/\pi)} & \mathrm{D} = \{\text{diameter of a defined number of strands}\} \end{array}$$

Just as with the solid core wire, the diameter of the multi-stranded wire is then compared to a wire gauge chart to determine the size of the wire.

The metal composition of a wire is typically copper. In some instances, it can be coated with tin to protect the wire from oxidation; such wire is called tinned-copper wire. While copper wire is most frequently encountered in IEDs, wire may be composed of alloys or other metals such as aluminum or steel. Examination of the metal in the wire can be performed using XRF or SEM-EDS. By calculating the size and metal composition, examiners can provide law enforcement officers with information to develop investigative leads in their search for the original source of the wire used in the explosive device. Comparisons can be made to wire either collected through a search warrant of a suspect's property or purchased where it was originally sold if the wire type is unique.

In some instances, the insulation covering the wire may have markings describing its properties. Wire recovered from the Boston Marathon Bombings had "STYLE 3135" marked on the insulation, which was consistent with a single conductor, silicone rubber insulation. If the wire is not marked by the manufacturer, the insulation material can be determined by analyzing the material using FTIR or Raman.

If the wire does have markings describing its properties, it should also be marked with the manufacturer's name or possibly an alphanumeric code which has been assigned to the manufacturer by an accrediting organization. Underwriters Laboratories (UL), an accrediting organization which certifies wire for commercial use, assigns a unique E-number (E and a three to six-digit number for wire and cable products) to each applicant in every product category. The wire recovered

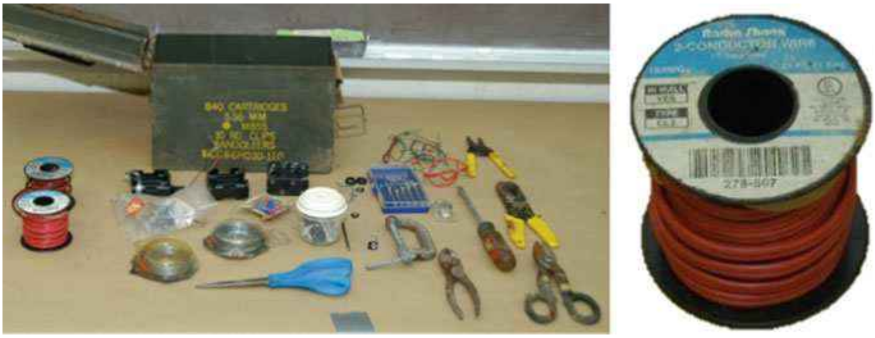


Fig. 9.15 Contents of ammunition can buried by Eric Rudolph (left), close up of wire spool recovered (right) which could be compared to wire evidence collected from the post-blast scenes linked to Rudolph

from the Boston Marathon Bombings had “E336285” marked on the insulation. When looking up this E-number on UL’s Web site, the wire was determined to be manufactured by Dongguan ZhongZheng Wire and Cable Tech Company Limited. Once the manufacturer is determined, it may be possible to establish where the wire was originally sold.

Examination of wiring was significant in the case of serial bomber Eric Rudolph. As part of a plea agreement, he told authorities where to find more than 250 lb of dynamite and other materials buried at sites throughout North Carolina. These items were found on April 5, 2005, in a rural area known as Unaka in the Nantahala National Forest. Under the stump of a fallen tree, authorities found two buried ammunition cans containing a variety of items, including two spools of wire (Fig. 9.15).

9.4.4 Batteries

When analyzing a battery used in an explosive device, a forensic examiner may determine the manufacturer or distributor of the battery, the type of battery, and markings associated with the expiration date and manufacturing date of the battery, as shown in Figs. 9.16 and 9.17. This information is noticeable on the metal casing covering the battery; however, it may not be easy to determine some of these markings since the manufacturer may use codes only known to them. Once all of the markings from the battery have been obtained, the forensic examiner should contact the manufacturer directly in order to decipher the meanings of all codes that are unknown from the initial examination. By knowing the manufacturing codes, it may be possible to determine the location where the battery was originally purchased. Depending on circumstances, an examiner may also determine whether the battery as received is in working order by testing its voltage.

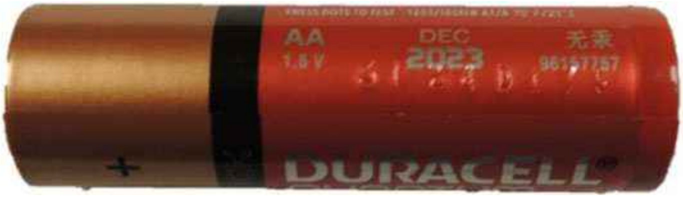


Fig. 9.16 A Duracell® Quantum AA alkaline battery. While the expiration date of December 2023 is clearly visible on the battery, the manufacturer's code of "3F24D179" can only faintly be seen stamped into the battery label

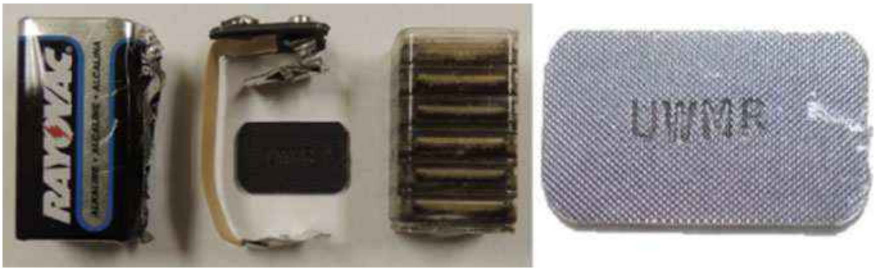


Fig. 9.17 Components of a Rayovac® 9V alkaline battery (left). The base of the battery had manufacturer's code of UWMR (right) which was identified by Rayovac® as being manufactured on November 13, 2011, by Gold Peak Industries in Malaysia

In most explosive devices, the battery tends to be relatively small in size, with just enough energy output to function the initiator. Commonly encountered batteries used in explosive devices include AAA, AA, and 9 V; however, the size of the battery is really up to the discretion of the builder. The battery recovered from the Atlanta Centennial Park Bombing in 1996 was an EVEREADY® 12 V lantern battery, which was used to initiate an electric match inside each of the three pipe bombs inside the backpack. In some instances, the battery used in an explosive device can be specifically linked to a commercial product. Batteries recovered from the Boston Marathon Bombings were C cell in size and had "Tenergy® 3000" marked on the outer casing. The batteries, as well as the plastic holder which housed them, were identified as a 7.2 V battery pack for a remote-control car.

When encountering a post-blast scenario, the internal battery components and outer casing will generally survive the explosion; however, the battery may be fragmented into several parts. From the collected evidence at the scene, the forensic examiner will need to recognize the internal components of the battery. Since there are so many different types of batteries and the internal components differ for each manufacturer, it may be necessary to purchase similar exemplar batteries to positively identify the internal components collected at the scene.

9.4.5 Containers

A container is a very common component of an explosive device, whether it is used for transport or concealment, as with a backpack, or as confinement for a low explosive, as with a pipe bomb. In some instances, the container can be used to entice an individual to unknowingly activate the explosive device. In March of 2012, three pipe bombs hidden inside of flashlights exploded in the Phoenix area, causing minor injuries to five people. The bomber knew that when the flashlights were found, an unsuspecting individual would likely push the on/off button to see if it worked. Depending upon the intended target of the bomber, a limitless selection of containers can be utilized in the construction of an IED. Below is a list of some other types of containers that have been used in the construction of IEDs:

- Bag/backpack/briefcase
- Box/package
- Metal/plastic can
- Pipe/tube/fitting
- Propane cylinder
- Tennis ball
- Bottle/jug/jar
- Compressed gas (CO_2) cylinders
- Cardboard tube
- Pressure cooker
- Suitcase
- Vehicle

Since commercial low explosives are much more accessible than high explosives, explosive devices consisting of a threaded pipe (or pipe nipple) sealed on each end with an end cap (as seen in Fig. 9.18) are most often encountered in casework in the USA. Pipes can be purchased from a number of sources, are inexpensive, and have the ability to explode when they exceed their maximum allowable pressure, especially from the combustion of a low explosive sealed within. Pipes and fittings, which include pipe nipples, end caps, elbows, tees, unions, reducers, and plugs, are sold in a variety of types and sizes. Metal pipe and fittings sold in retail stores include galvanized steel, copper, brass (used in potable water systems), and black steel (used in residential gas supply). Of these types of

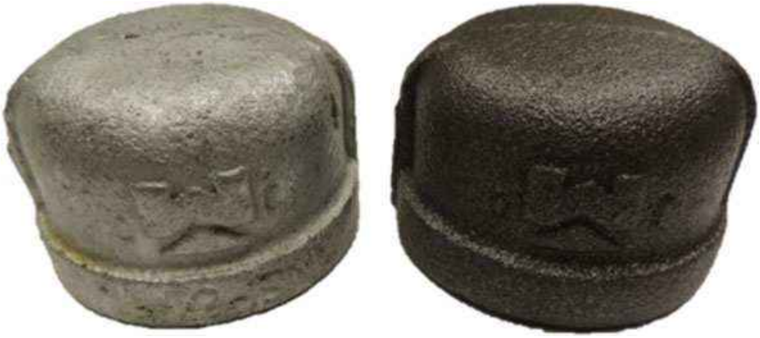


Fig. 9.18 Two 1-inch nominal diameter cast iron end caps. Galvanized (left), black finish (right). Mueller Industries, Incorporated logo visible on both

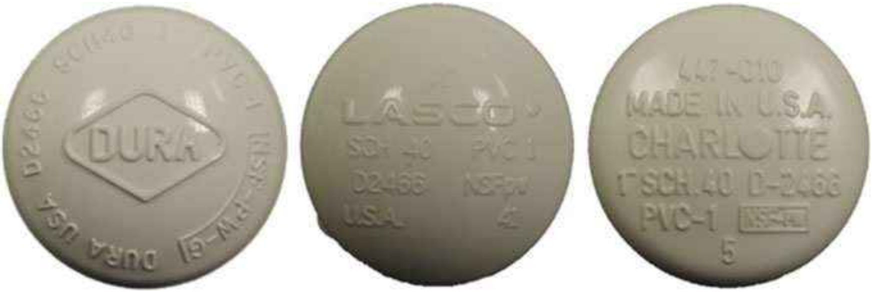


Fig. 9.19 Faceplates of three 1-inch nominal diameter PVC slip-on end caps

metals, galvanized and black steel pipe, and galvanized and black iron fittings are most often used in explosive devices due to the large variety of sizes that can be purchased and ease of modifying to create an IED. Brass fittings are costly and limited in sizes, and copper pipe is usually sold in lengths that need to be altered before it can be utilized.

Plastic pipe and fittings sold in retail stores consist of: white polyvinyl chloride (PVC); chlorinated PVC (CPVC); acrylonitrile butadiene styrene (ABS), which are used in either potable water systems or drainage, waste and vent (DWV) systems; and gray PVC, which is used in electrical conduit piping. Of these types of plastics, white PVC is most often used in explosive devices due to the large variety of sizes and fittings that can be purchased. CPVC and gray conduit PVC are not as widely sold as white PVC, and ABS, since it is primarily used in DWV systems, is generally sold in sizes of 2-inch nominal diameter or larger. Most pipe bombs encountered in explosive investigations have a diameter less than two inches.

The American Society for Testing and Materials (ASTM) and the National Sanitation Foundation (NSF) are organizations that test and rate piping materials for use in certain applications. For all pipes and fittings, approved identification markings, such as those shown in Fig. 9.19, must be visible on the exterior. This may not seem important to most people; however, the information on the fittings can possibly lead to where it was originally purchased. When it comes to a post-blast scene involving a pipe bomb, it is crucial that a thorough processing of the scene takes place in order to collect as much of the original container as possible. Once in the laboratory, it is the responsibility of the forensic examiner to identify which manufacturing codes and markings can assist in determining the origin.

9.4.6 Tapes and Adhesives

Quite often tape and adhesive are used in the construction of an explosive device, from positioning various components together to securing enhancements to the outside of the container. Tape is available in a variety of sizes, colors, and types and has the potential to capture forensic clues which can identify the bomb builder (see Chap. 11). Latent print examiners have been able to identify fingerprints on both the adhesive and non-adhesive portions of various types of tape, and pieces of tape may also be a good source of potential DNA, hairs, fibers, or other trace evidence unique to the bomb maker's environment. In addition, trace examiners have been able to fracture match the ends of tape removed from an explosive device to a roll of tape found during a search warrant. When analyzing tape recovered from a post-blast scene, it is crucial to microscopically examine the fragments. Intact explosive particles and post-combustion residues may stick to the adhesive portion of the tape, which may be the best source for identifying the explosive used in the device. If collected carefully, the post-blast residue will be minimally affected by the adhesive portion of the tape.

Adhesives can be used in the construction of an explosive device in a similar fashion as tape. Common purposes for adhesives on an explosive device are the securing of a pyrotechnic fuse into an end cap with hot melt glue, attaching metal enhancements to the outer surface of a pipe using superglue, as well as the joining of a plastic pipe and end cap together with PVC cement in the construction of the container. While these are a few examples of adhesives that can be used for these applications, the bomb builder has the ability to choose from a large variety of adhesives that can be purchased from a number of merchants.

9.4.7 Enhancements

Enhancements are added to an explosive device to increase the lethality and damage it may cause. Enhancements may consist of pressurized vessels, ignitable liquids or gases, or added fragmentation. During the 1993 World Trade Center Bombing, terrorists placed three compressed tanks of hydrogen gas inside a Ryder van which housed the urea nitrate main charge. A similar enhancement was used in the Columbine High School attack on April 20, 1999, where two explosive devices equipped with propane tanks (shown in Fig. 9.20) were placed inside the cafeteria. The timers on both devices were set to function at 11:17 am, which was the start of the school's first lunch session [5]. Fortunately, both devices failed to function; otherwise, it would have greatly increased the overall casualties in the school massacre.

In most instances, enhancements will consist of metal, plastic, or glass articles that are added to increase the lethality of the explosive device. This added material may be referred to colloquially as **shrapnel**; some agencies also refer to this material as **fragmentation**. The enhancements may consist of nails, screws, nuts, washers, ammunition shot, glass marbles, or any other items deemed capable of producing damaging projectiles by the bomb builder. The added objects can be taped or glued to the outside of the explosive device, as in Fig. 9.21, or placed loosely inside of the device with intimate contact with the main charge.

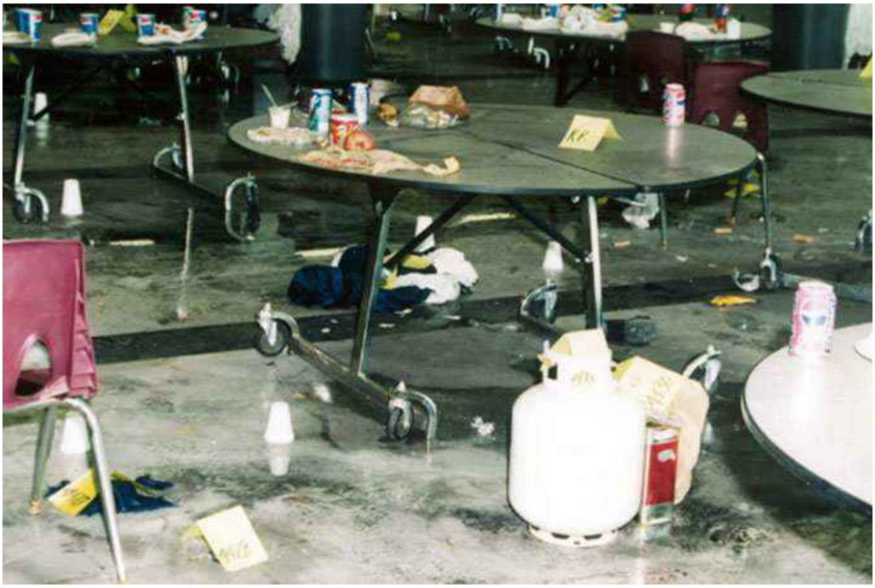


Fig. 9.20 Explosive device recovered from the cafeteria in Columbine High School. [Courtesy of Jefferson County Sheriff's Department]

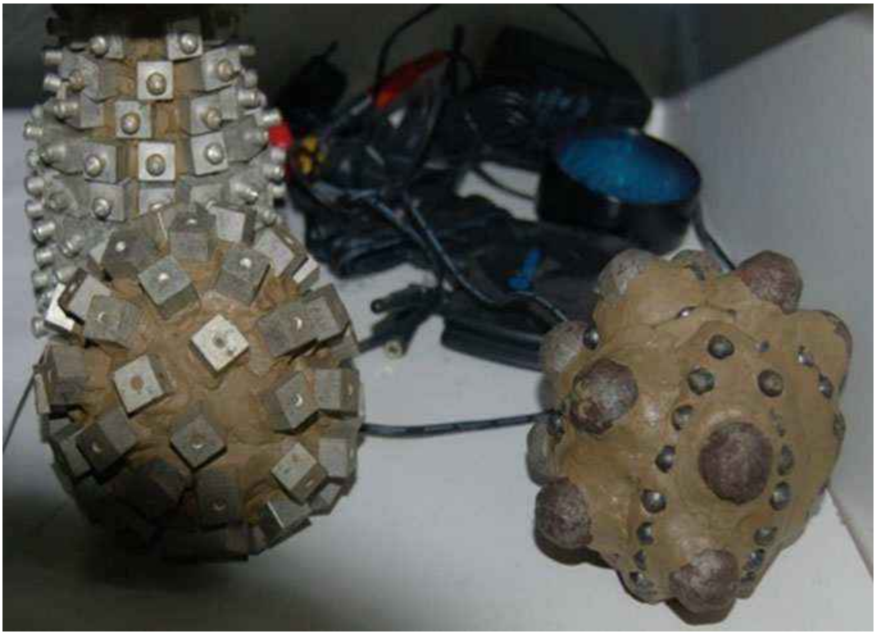


Fig. 9.21 Improvised explosive devices seized from a home in Escondido, California, in 2010. [Courtesy of San Diego County Sheriff's Department]

If materials such as screws, nuts, or nails are found during the course of the investigation, it is important to identify the type or use, size, and any manufacturer markings which may lead to the origin of the identified components. Ammunition shot can be metal, glass, or plastic and is sold in a variety of colors and sizes. Metal shot can be lead or steel, which can be coated in copper or zinc to prevent corrosion.

9.5 Limitations of Device Examinations

Based on the results of analyses conducted throughout the five steps previously described, a device examination may result in a variety of conclusions. Each agency and jurisdiction will have its own standards for what examiners may and may not opine. Further, the conclusions that can be reached will depend on what is submitted. An examiner may be able to determine that a partial or complete device was recovered. The examiner may also potentially be able to identify how such a device would have functioned. It is also possible that no viable device is present.

An examiner might also be asked to analyze a set of bomb-making instructions or schematics to determine if the instructions would produce a viable device or a device such as one that was located. If a device or series of devices have already been analyzed, the examiner may need to determine if the device(s) or device componentry found later, perhaps during the execution of a search warrant or from another event, is similar to any that have already been analyzed. The degree and strength of an association between components will vary depending on circumstances. For example, two pieces of wire may not have as strong an association as two circuit boards taken from identical phones.

Although components may be identified as part of a general class (e.g., Exhibit 1 was identified as a length of PVC pipe), device analysis does not typically lend itself to definitive associations; for example, laboratory analysis cannot generally determine a specific source of an IED component or link an item uniquely to a suspect, as with DNA, fingerprints, or toolmarks. It can never be said that the length of PVC pipe found as part of an IED was "identified" as having come from a suspect's house without an end-to-end physical match. The best that can generally be inferred is that the length of pipe found in an IED was consistent in size, appearance, chemical composition, etc., with pipe found in a suspect's residence.

Examination of post-blast evidence can face extreme limitations which will vary on a case-by-case basis. The devastation to the physical surroundings imparted by explosives will often make any useful examinations impossible on items of evidence. In all cases, the examiner must determine which examinations are appropriate based on what items have been deemed of forensic value.

Examiners may not testify to the intent of the bomber. They may render opinions on the logical usage of components or the practical aspect of modifications made in producing a device. For example, an examiner may not state that it was the bomber's "intent" to increase lethality of their bomb by adding hardware to the exterior of the device. However, they may state that this is often discussed in bomb-making literature as an addition to explosive devices to increase their lethality, and that it has been scientifically proven to increase the lethality of an explosive device.

9.6 Summary

Devices encountered during casework come in a wide variety of types ranging from simple pipe bombs to highly sophisticated electrically fuzed IEDs. The examination of these devices has a very basic focus. Forensic examiners analyzing any IED strive to find out what the IED was constructed from, where the pieces used to manufacture the IED originated, and how the device functioned. Since an IED can be made from just about any item accessible to a bomb builder, the forensic examiner must be prepared to analyze a broad spectrum of componentry. Knowing the core components of power source, load, conductor, and switch will guide examinations, but the damage done to a fuzing system by an explosion will introduce unique challenges to examiners striving to gain insight into the evidence in front of them. The principles outlined in these sections provide the general logic applicable for all other analyses brought to bear in the field of IED forensics.

9.7 Questions

1. What are the four major components of an electric fuzing system and name an example an examiner may find of each?
2. What are the five basic steps used by a forensic examiner when analyzing evidence submitted for examination?
3. What types of things may be found with an IED that are not part of the fuzing system?
4. An IED is recovered which employs a pink ammo can and a MegaCharge brand 9 V battery. The empty packaging for a MegaCharge 9 V, a bottle of pink spray paint and an identical ammo can were found during subsequent searches of a suspect's house. Has the source of the IED been identified? Why or why not?

References

1. Krizay GD (2018) Department of defense forensic science lexicon. Defense Forensics and Biometric Agency. Available via DFBA. http://www.dfba.mil/documents/DoD_Forensic_Science_Lexicon.pdf. Accessed 20 July 2018
2. Office of the Law Revision Council United States Code (2018) 18 USC 921: Definitions. http://uscode.house.gov/view.xhtml?req=granuleid:USC-prelim-title18-section921&num=0&edition=prelim. Accessed 20 July 2018

3. Image provided by DePhogration Digital Image Capture & Photography. Knife switch modelled after https://openclipart.org/detail/295450/knife-switch
4. Chef AQ (2015) Designing a timed hand grenade. Inspire Magazine 14:72–81
5. Cullen (2017) The columbine guide. https://www.columbine-guide.com. Accessed 23 July 2018

Dr. Kirk Yeager is Chief Explosives Scientist for the FBI. He has over 25 years of experience in energetic materials analysis, research, and testing. Since 2000, he has specialized in the investigation of bombing matters with a focus on forensic examination of explosive and hazardous devices. He has provided forensic assistance and advanced training to law enforcement partners in dozens of countries, produced over 75 specialty publications in the area of explosives and IED's, and authored 3 scientific textbook chapters.

John Jermain is a forensic chemist with the Bureau of Alcohol, Tobacco, Firearms and Explosives. Mr. Jermain specializes in the analysis of commercial and homemade explosives, as well as the forensic analysis of improvised explosive devices. Mr. Jermain also provides explosive training to Federal Agents, Military personnel, and bomb technicians throughout the United States.

Chapter 10
Bridging Explosives and Fire Debris Analyses

Michelle Evans

Learning Objectives

- Understand what explosives and fire debris cross-disciplinary cases are.
- Understand the types of materials that may be identified in these cases.
- Understand various analytical schemes and results for cross-disciplinary cases.
- Understand the reporting considerations.

10.1 Introduction

Cross-disciplinary cases are cases that require examinations in multiple disciplines. For the purposes of this chapter, it will refer to cases needing both ignitable liquid and explosive testing (e.g., **ANFO**) or cases that could fall in either one, like **incendiary mixtures** (e.g., **road flares**). Fire debris and explosive analyses are separate specialties, requiring a different knowledge set and training program. Many laboratories, primarily state and local systems, include fire debris and explosives under the "trace evidence" umbrella, allowing examiners to analyze almost any type of evidence submitted. However, some laboratories, such as those in federal agencies, have examiners that are experts in only one of these sub-disciplines of trace.

Ideally, an examiner would be able to handle all cases in the trace evidence discipline, but this necessitates significant training in multiple areas. Learning about the manufacturing processes, history, instrumentation, analysis, and data interpretation in each sub-discipline is imperative for examiners testifying in court. The amount of information can be overwhelming and may lead to examiners only barely

---

M. Evans (✉)
Bureau of Alcohol, Tobacco, Firearms and Explosives, Ammendale, MD, USA

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_10

scratching the surface of the recommended knowledge base. Alternatively, laboratories may choose to have examiners specialize in just one or two facets of the many fields in the trace discipline. While these individuals are considered experts in their fields, they are often not able to analyze every case. Thus, a case that might be able to be handled by one person at one laboratory would instead need to be examined by two or more at another laboratory.

Regardless of whether one or two examiners handle a cross-disciplinary case, the order of analyses is extremely important. When a case requires both fire debris and explosive testing, if the evidence packaging is appropriate, then the ignitable liquid analysis must be conducted prior to explosive analysis, to avoid any potential loss of ignitable liquids. If there are concerns regarding organic high explosives, headspace extraction temperatures and times can be adjusted to allow for the potential detection and identification of both organic high explosives and ignitable liquids.

10.2 Explosives

While many oxidizer–fuel mixtures are solid, as discussed in Chap. 7, the “fuel” in an explosive oxidizer–fuel mixture can be an ignitable liquid. The most notable example of this type of mixture is **ANFO**. Analysis of this material requires identification of the ammonium nitrate oxidizer, as well as the fuel oil, which is a heavy petroleum distillate (HPD). It is also possible that an individual may combine ammonium nitrate or other oxidizers, like potassium chlorate, with another type of ignitable liquid, ranging from gasoline to biodiesel; the examiner must be able to know the difference between them in order to properly classify and identify the material. Other potential liquid fuels include nitromethane, nitroethane, nitrobenzene, alcohols, and lubricating oils, such as baby oil or mineral oil [1]. With the exception of the oils, the other listed fuels are considered ignitable liquids as defined by ASTM E1618 Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography–Mass Spectrometry [2].

For intact samples, analysis is relatively straightforward (see Chap. 7). The oxidizer can typically be identified using a combination of a variety of techniques, such as elemental analysis (SEM-EDS or XRF), XRD, FTIR, Raman, and/or PLM (Fig. 10.1). The fuel is most commonly identified using GC-MS (Figs. 10.2, 10.3 and 10.4); however, FTIR may be appropriate for compounds like nitromethane (Fig. 10.5). High-temperature GC-MS may be necessary for the differentiation of heavy molecular weight oils and waxes, as discussed in Chap. 2 [3–8]. If the sample appears wet and/or has a petroleum-like odor, a solvent extraction of the sample may be warranted in order to remove the fuel for analysis. Solvents such as pentane and hexane would be suitable for most ignitable liquids. Alternatively, passive headspace concentration (PHC) with a charcoal strip or solid-phase

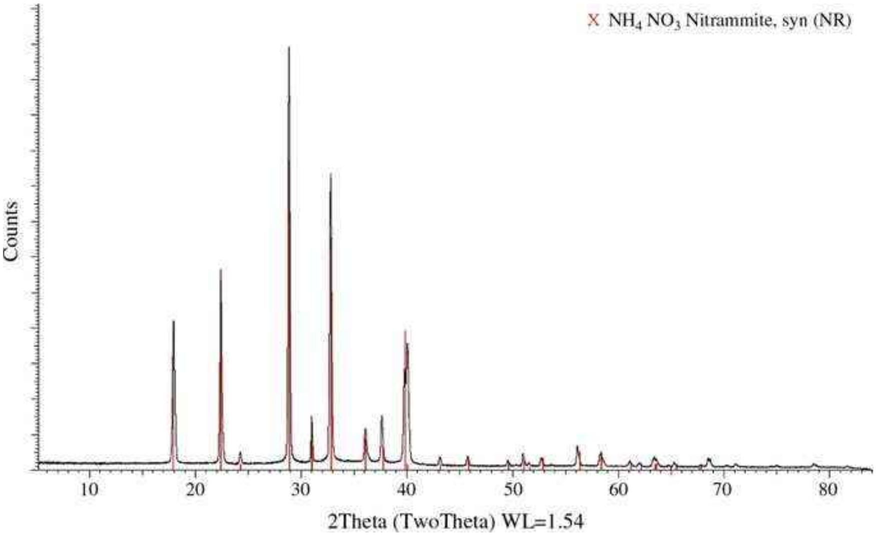


Fig. 10.1 X-ray diffraction pattern of ammonium nitrate

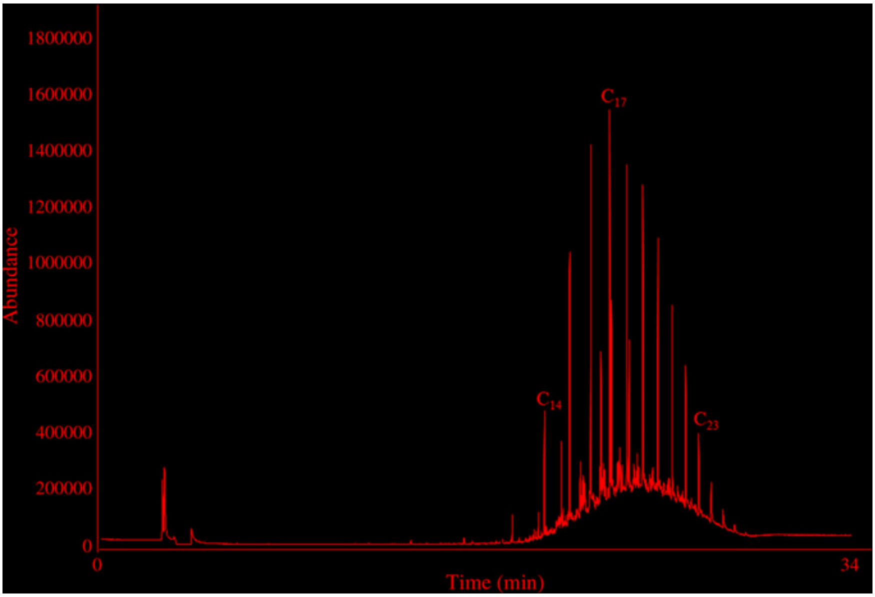


Fig. 10.2 GC-MS data of fuel oil from an intact mixture with ammonium nitrate

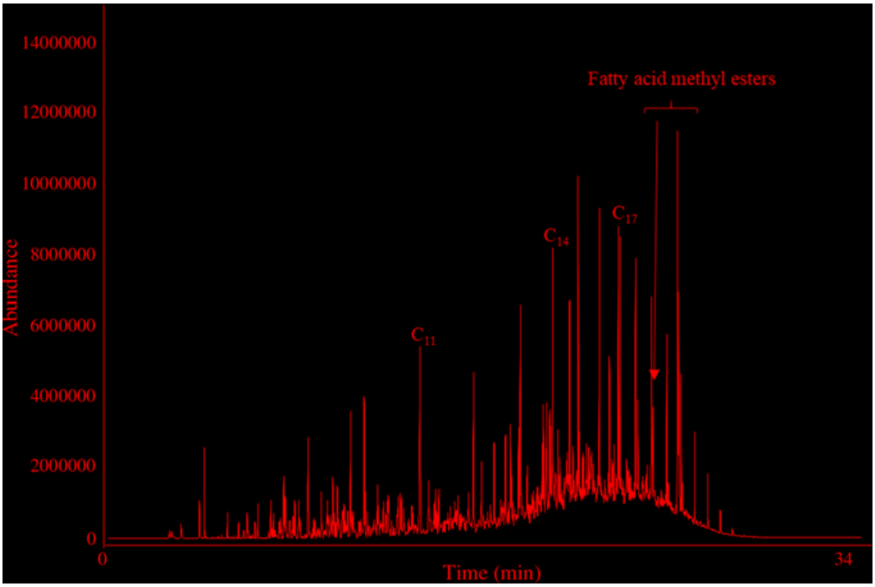


Fig. 10.3 GC-MS data of biodiesel from an intact mixture with ammonium nitrate

microextraction (SPME) could be utilized to extract the ignitable liquid vapors from the sample.

Post-blast analysis of oxidizer and ignitable liquid fuel mixtures is more challenging, given that the fuels are usually completely consumed, and there is very little oxidizer residue remaining. Since a typical **ANFO** mixture is 94% ammonium nitrate (AN) and 6% fuel oil [1], the quantity of fuel after a blast will be negligible. Also, except for the fuel oils (HPDs) and lubricating oils, the other liquid fuels listed above are volatile enough that they would evaporate quickly, following an explosion.

If post-blast device fragments are submitted and appropriately packaged in vapor-tight containers for ignitable liquid testing, then the fuel may be extracted using PHC or SPME, followed by GC-MS analysis (Fig. 10.6). As mentioned previously, if volatile organic high explosives are also suspected, headspace extraction temperatures and times can be adjusted so that both the ignitable liquids and explosives can be identified (this will be discussed more extensively in Sect. 10.4). After headspace extractions, then the fragments should be evaluated for residue that can either be physically removed or rinsed with water, as with other post-blast evidence as discussed in Chap. 8 [9, 10].

Further challenging the post-blast examination and conclusions are the potential for the oxidizers and fuels to be found inherently in nature and/or in certain

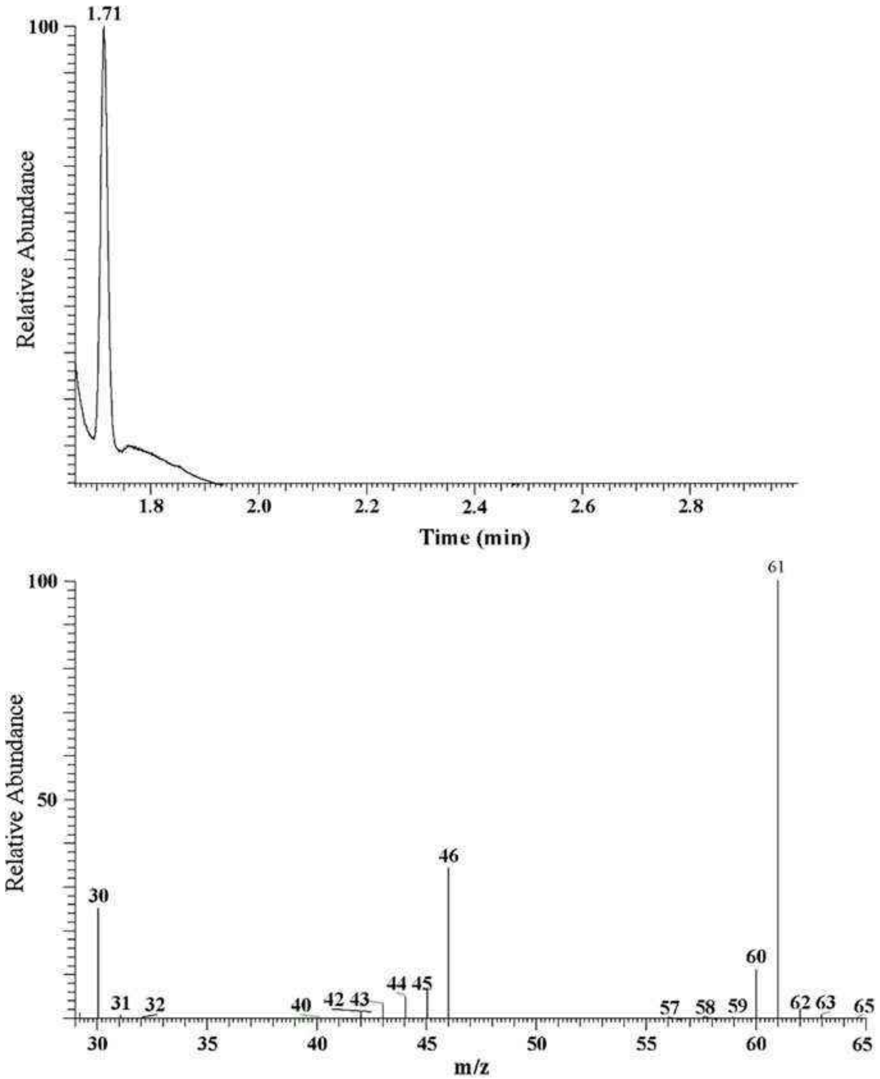


Fig. 10.4 GC and MS data for nitromethane

substrates. For example, submission of dirt from a blast seat/crater may contain ammonium nitrate or another similar oxidizer from fertilizer or fuel from a vehicle or heating oil tank leak. Examiners should be cautious when interpreting post-blast results where oxidizers and ignitable liquid fuels are suspected and consider alternative potential sources, other than solely from an explosive mixture.

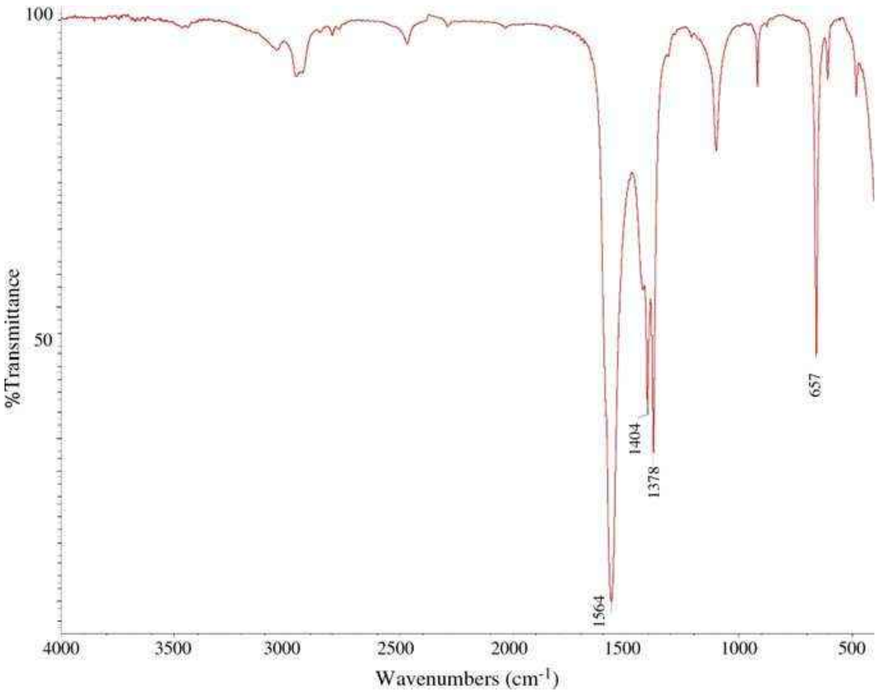


Fig. 10.5 Nitromethane by FTIR

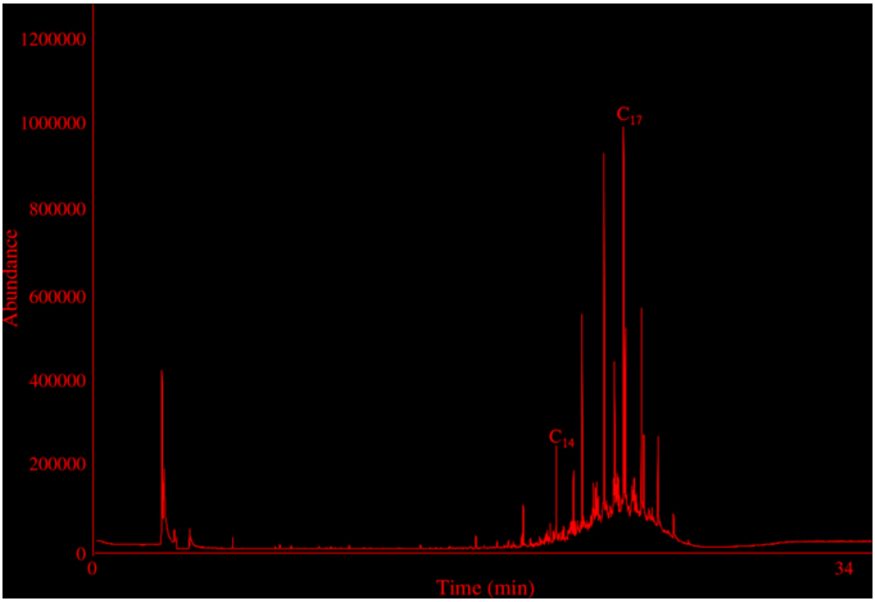


Fig. 10.6 GC-MS data of fuel oil from a post-blast scene collected using passive headspace concentration

10.3 Incendiary Mixtures

Incendiary mixtures are materials that will cause a fire or a thermal event instead of an explosion. These mixtures should not be confused with incendiary devices, which are discussed briefly in Chap. 2. Typical incendiary mixtures include **road flares**, **thermite**, and **hypergolic mixtures** [11]. These types of mixtures may fall in either the explosive or fire debris discipline, depending on their end use and configuration. For example, a road flare could be used as is to start a fire, but if the powder is removed and confined in a pipe, then it could function as a low explosive.

Road flares, also known as **fusees**, typically contain strontium nitrate, along with other possible oxidizers such as potassium nitrate, potassium perchlorate, and fuels that include sulfur, sawdust, and a polymeric binder [12–15]. Oxidizers and at least some of the fuels from intact material, whether from an incendiary or explosive investigation, can be identified using techniques mentioned previously (Fig. 10.7).

Sold as is, **road flares** are in a cardboard tube and many come with a metal stand to prop up the flare while it is in use (Fig. 10.8). When **road flares** burn, the cardboard burns with the flare contents, and the remaining residue will be white powdery residue (Fig. 10.9).

Often, post-fire, the metal stand or spike will be present as well. Reaction products present either post-fire or post-blast can include, but are not limited to, strontium carbonate, potassium carbonate, potassium sulfate, strontium chloride, potassium chloride, and potassium chlorate. These compounds or their ions can be identified with a variety of techniques, such as those already mentioned above

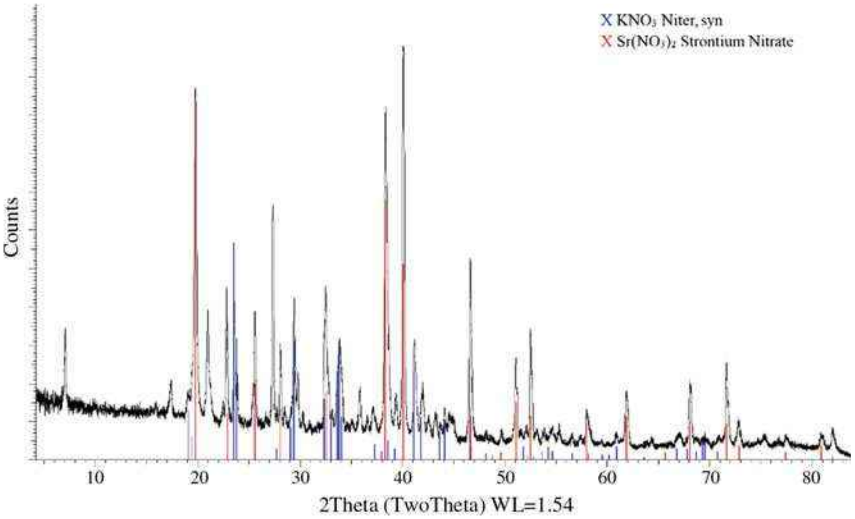


Fig. 10.7 X-ray diffraction pattern of potassium nitrate and strontium nitrate from an intact road flare

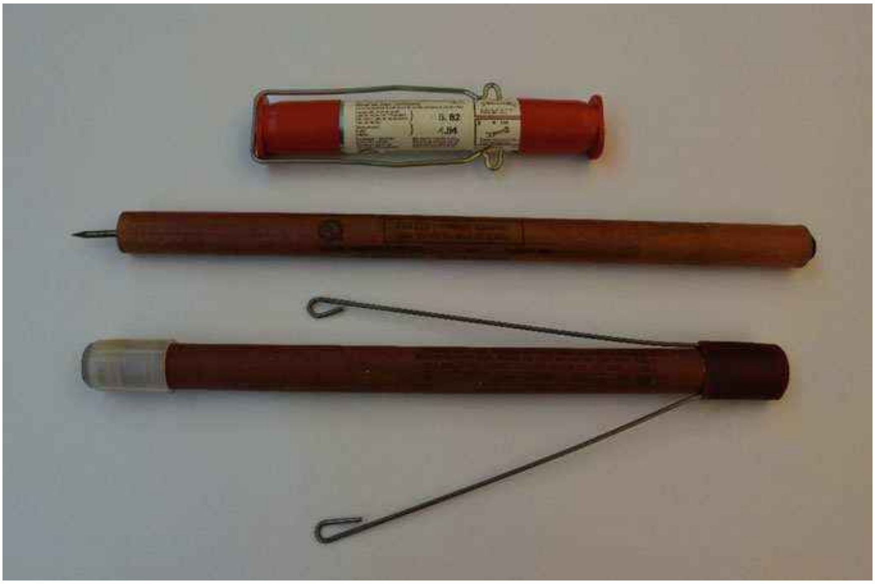


Fig. 10.8 Examples of intact road flare containers

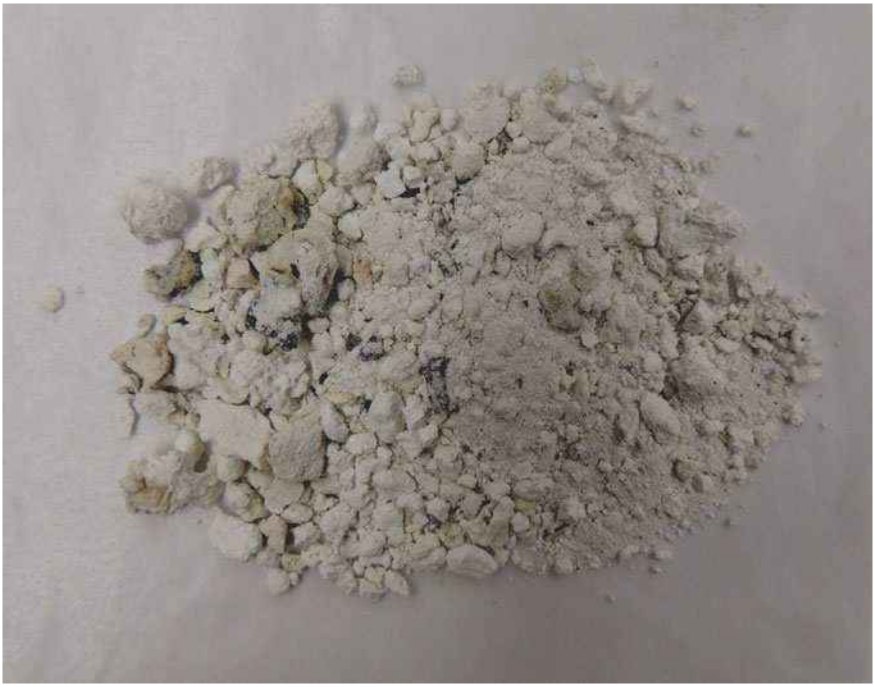


Fig. 10.9 Post-burn residue from a road flare. Photograph courtesy of Dr. Katherine Hutches

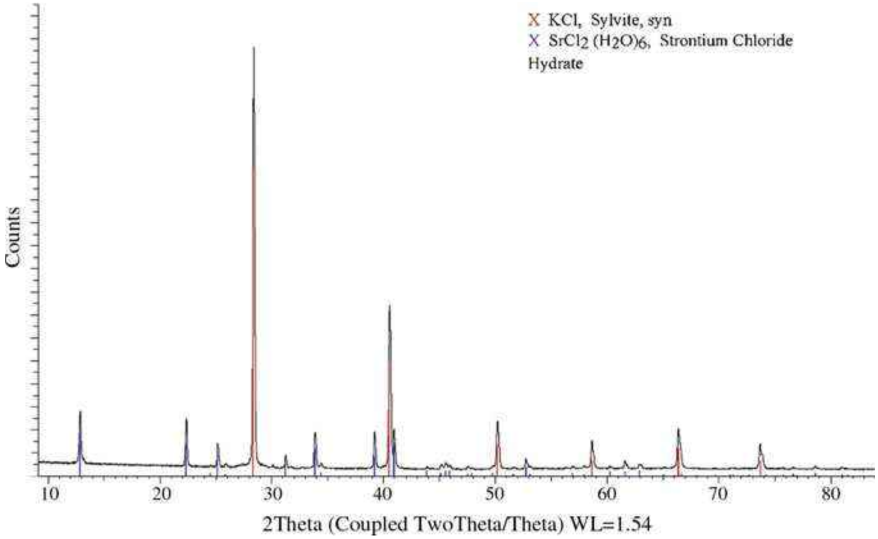


Fig. 10.10 X-ray diffraction pattern of road flare residues' post-burn

(Fig. 10.10). Interpretation of the results will depend on what type of evidence was submitted to the laboratory. For example, identification of strontium carbonate and potassium sulfate in white powder from a fire scene, along with potential remains of a cardboard tube and the metal stand, can result in a report stating that the residues of a road flare were recovered or similar language. However, if the same compounds were identified in a post-blast pipe, then the report could state a variety of conclusions, such as residues chemically consistent with a road flare were recovered or residues of a pyrotechnic composition were recovered. Appropriate wording will depend on what was identified as well as laboratory policy.

Match heads are commonly found in devices, often with their wood or paper sticks removed. For "strike anywhere" matches, which typically have a white tip, the heads may contain potassium chlorate, red phosphorus, and sulfur. With "safety" matches, the phosphorus is located on a separate strike pad or strip either on the side of the box or on the paper matchbook. Match heads can be considered oxidizer and fuel mixtures, the analysis of which has been discussed in Chaps. 7 and 8. However, identification of phosphorus is difficult via FTIR and XRD. The best methods for phosphorus include elemental techniques and Raman.

Thermite and **thermate** are incendiary mixtures that contain a metal and a metal oxide that generate more of a heat-producing reaction than an explosive event when initiated. **Thermate** is used in incendiary grenades and contains additional oxidizer, such as barium nitrate. Both **thermite** and **thermate** produce a molten slag that has found legitimate use in the welding industry. While aluminum and iron oxide are the most common constituents of **thermite**, other materials, like the aluminum and magnesium alloy magnalium, and metal oxides, such as lead oxide (red) and manganese dioxide, can also be used [12, 13]. When ignited, the reaction products will include an aluminum oxide and the corresponding metal. For example, if aluminum and iron oxide are used, then aluminum oxide and iron are produced during the reaction. Elemental techniques with XRD are good analytical instruments to use to identify these materials both pre- and post-ignition. Note that identification of iron-containing compounds can be difficult via XRD due to iron's fluorescence in an X-ray beam with a copper target. Additionally, it can be difficult to prepare post-combustion samples for XRD analysis. However, in the absence of XRD, chemical spot tests, FTIR, Raman, magnetic response, and PLM may provide information on the compounds present.

A **hypergolic mixture** consists of two or more materials that will ignite when mixed without an external ignition source [13, 16]. The most common **hypergolic mixtures** are brake fluid with pool chlorinator (usually calcium hypochlorite, also known as HTH), potassium permanganate with glycerin or glycol, and potassium chlorate with sugar and sulfuric acid [17, 18]. Other self-reacting mixtures can include gasoline and HTH and gas-producing **chemical reaction devices** [19–21]. The original ingredients and reaction products of these mixtures can be identified through a combination of the instrumental techniques discussed in Chap. 1. Visual examination of the evidence will often guide the examination schemes. While olfactory techniques are not encouraged due to the inherent health hazards, an odor can indicate the possible presence of chlorine, sugar, or a petroleum product, which may provide direction on analysis.

Pool chlorinator can react with most compounds containing a hydroxyl (–OH) group, such as ethylene glycol and rubbing alcohol (which contains isopropanol). The reactivity of this mixture increases with the number of –OH groups, such that polyols (with multiple hydroxyls), like brake fluid, are the most reactive, igniting rapidly (Figs. 10.11a, b). White, brown, and black clumps of wet material will

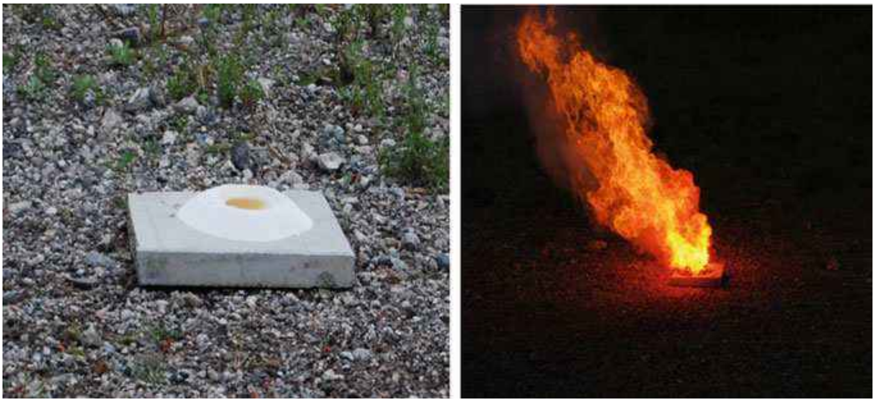


Fig. 10.11 A and B Brake fluid (glycol ether-based) and pool chlorine (calcium hypochlorite) mixture before and during reaction. Photographs courtesy of the Centre of Forensic Sciences, Toronto, Ontario

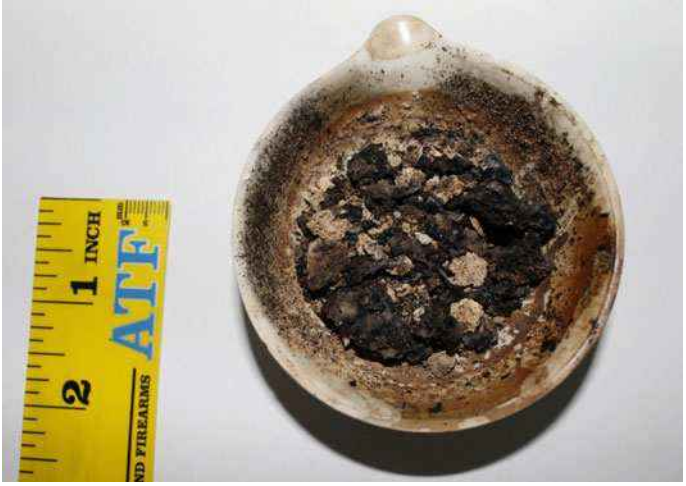


Fig. 10.12 Post-burn residue from a mixture of brake fluid and pool chlorine

remain after the incendiary event and often have a chlorine-like odor (Fig. 10.12). Both original components and reaction products may be identified, depending on the starting materials (Figs. 10.13, 10.14, 10.15, 10.16 and 10.17). Post-burn products for a glycol and HTH mixture can include calcium chloride hexahydrate, calcium carbonate, sodium chloride and/or sulfate, cyanuric acid, and chlorinated glycols [12, 17].

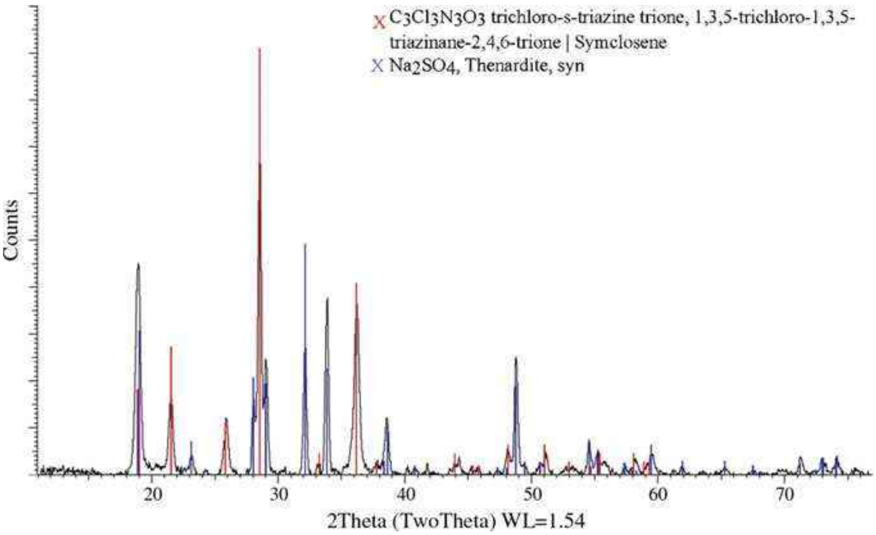


Fig. 10.13 X-ray diffraction pattern of an organic pool chlorinating powder known as Trichlor

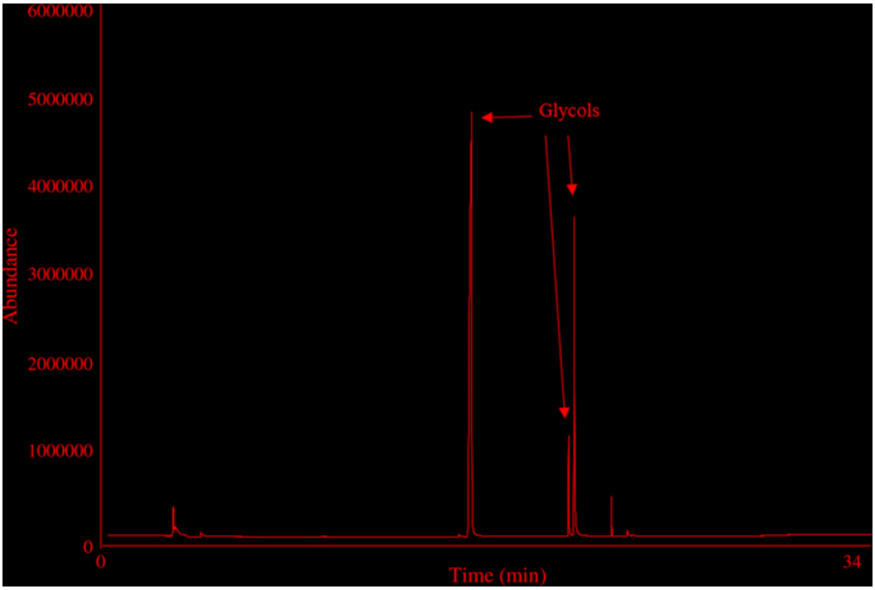


Fig. 10.14 GC-MS of one type of brake fluid

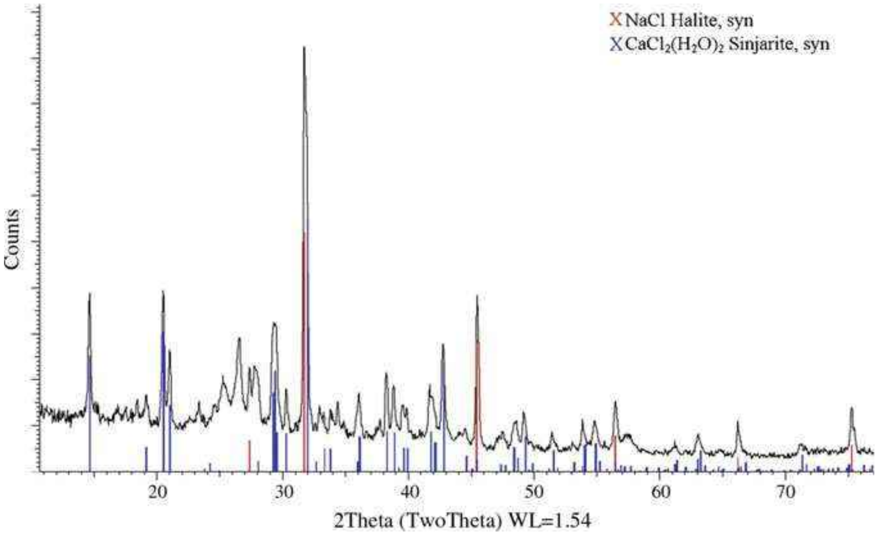


Fig. 10.15 X-ray diffraction pattern of post-reaction products from a mixture of inorganic pool chlorinating powder and brake fluid

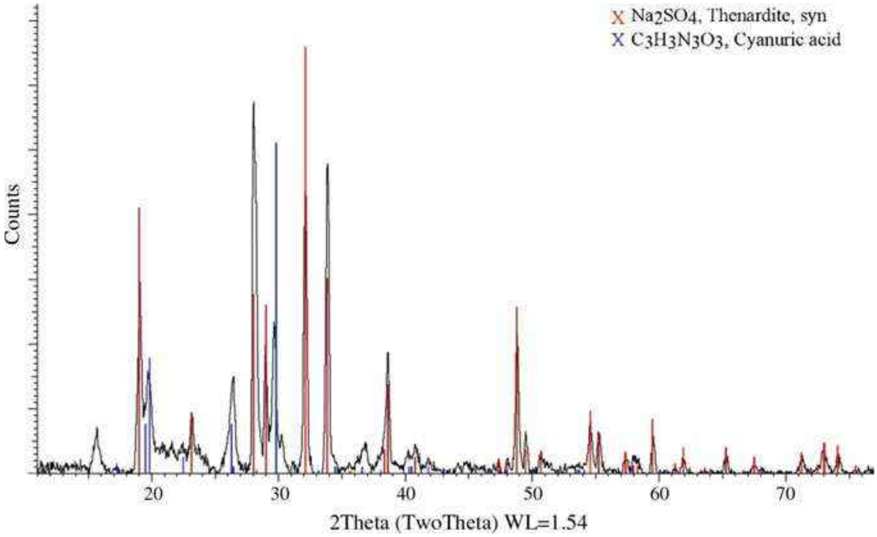


Fig. 10.16 X-ray diffraction pattern of post-reaction products from a mixture of organic pool chlorinating powder and brake fluid

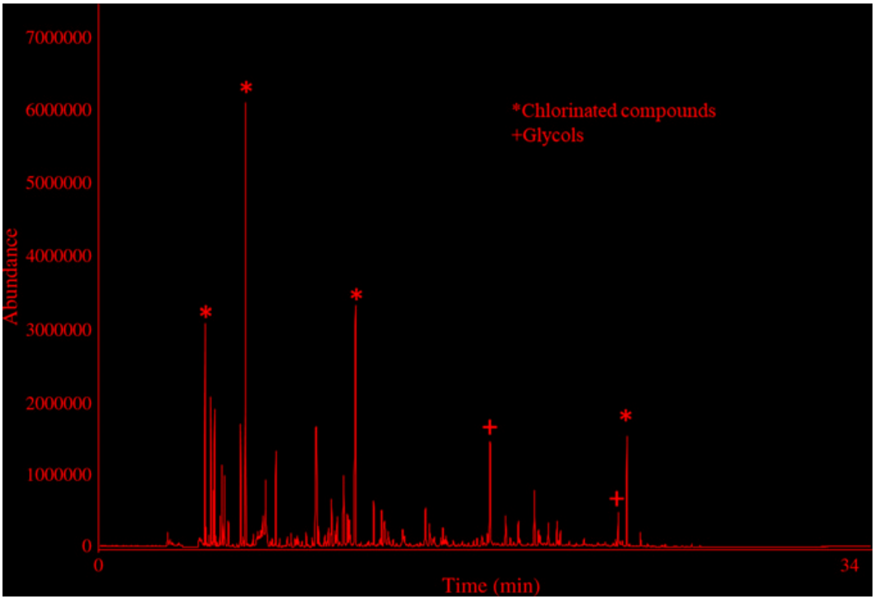


Fig. 10.17 GC-MS of post-reaction products from a mixture of pool chlorinating powder and brake fluid, collected using passive headspace extraction

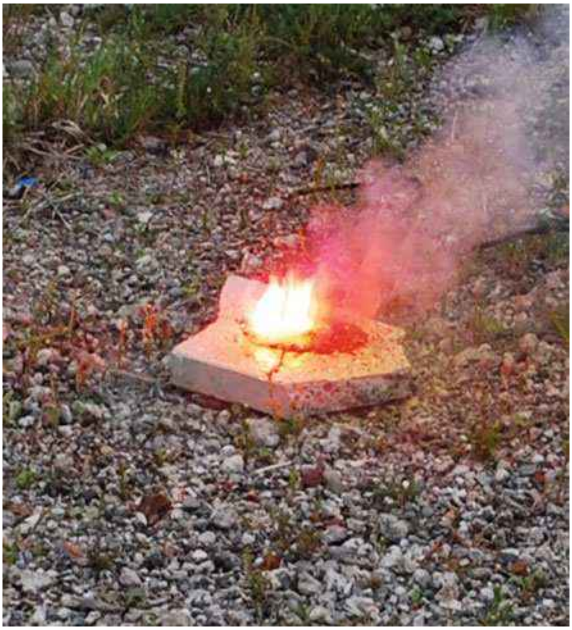


Fig. 10.18 Potassium chlorate, sugar, and sulfuric acid mixture. Photograph courtesy of the Centre of Forensic Sciences, Toronto, Ontario

Potassium permanganate and glycerin or glycol will not only ignite when mixed but will also cause an explosive reaction when confined. These materials, which are used for commercial fire starters to help with controlled burns, are balls of potassium permanganate that are injected with glycol [22, 23]. Potassium permanganate turns a brilliant purple when dissolved in water but generally has a black appearance when viewed with the naked eye. After an incendiary event, the residue will appear like soot and may be difficult to distinguish as material requiring analysis.

The mixture of potassium chlorate, sugar, and sulfuric acid has been used for self-igniting Molotov cocktails, as well as other incendiary devices [16, 18]. The sulfuric acid reacts with the potassium chlorate and sugar mixture to produce a brilliant reddish-pink flame and sparks (Fig. 10.18).

While analysis and identification of the self-igniting starting materials are relatively straightforward (Fig. 10.19), the reaction products may prove challenging to separate for examination. If a pungent odor or sludge-like material is noted in the evidence, headspace extraction for an ignitable liquid, followed by a simple pH test to determine acidity, should be done first, prior to any solvent extractions, to avoid inadvertently injecting strong acids onto chromatographic columns. After an explosive or incendiary event, sugar turns into a gummy, syrup-like material that can be difficult to identify, as recrystallization is impossible [11]. Extraction of the residue with water and analysis by LC or derivatization of the residue and analysis by GC-MS can identify the presence of sucrose, lactose, and glucose [24, 25]. IC and CE or IC-MS may be required to identify the original components. Depending

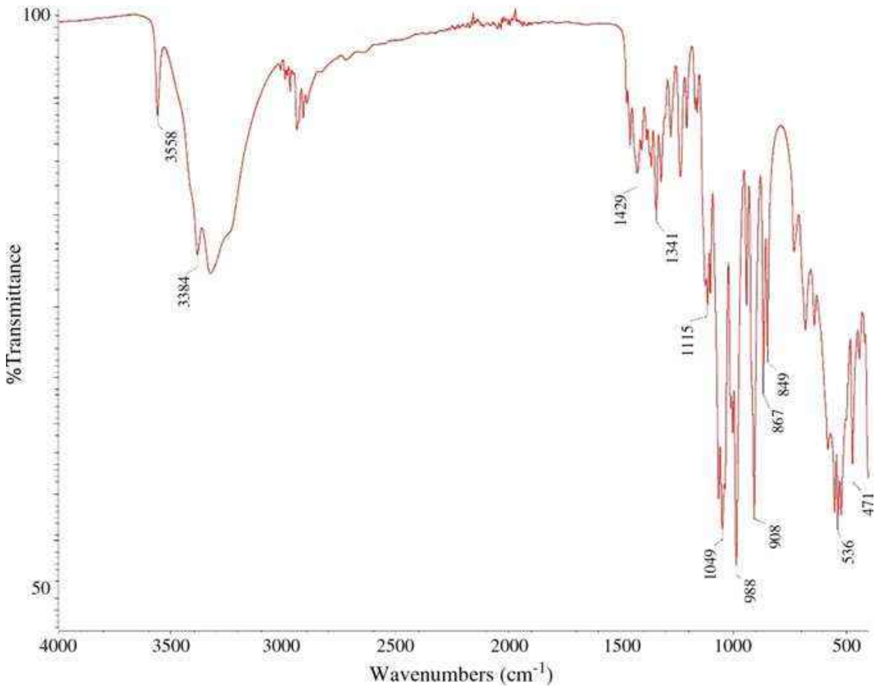


Fig. 10.19 Sugar (sucrose) by FTIR

on how much oxygen is present, reaction products could include potassium perchlorate and potassium chloride [1].

Another type of mixture that falls in between the fire debris and explosive sub-disciplines is the **chemical reaction device**. **Chemical reaction devices**, also known as acid bombs, bottle bombs, and “MacGyver” bombs, are manufactured from common household chemicals and produce a gas without an external ignition source [11, 20, 21, 26]. The reactions in these devices do not necessarily release large amounts of energy but are gas evolution reactions. When the reaction is confined, the buildup of gas increases the pressure. At high pressures, the container can fail catastrophically resulting in an explosive pressure wave release. The materials are typically confined in a plastic bottle (hence the name “bottle” bomb). These are self-initiating devices, since no external ignition source is needed for the reaction to occur. Typical materials used are dry ice, calcium hypochlorite with sugar or soda, hydrochloric acid with aluminum (usually aluminum foil), and sodium hydroxide or hypochlorite with aluminum (also known as a “Drano” bomb). If aluminum is used, then it is likely to be found either unconsumed or as a reaction product with the starting material. Elemental analysis, XRD, pH, chemical spot tests, and ion analysis can be utilized to determine the starting materials (Fig. 10.20), except in the case of dry ice, which will not leave an identifiable residue.

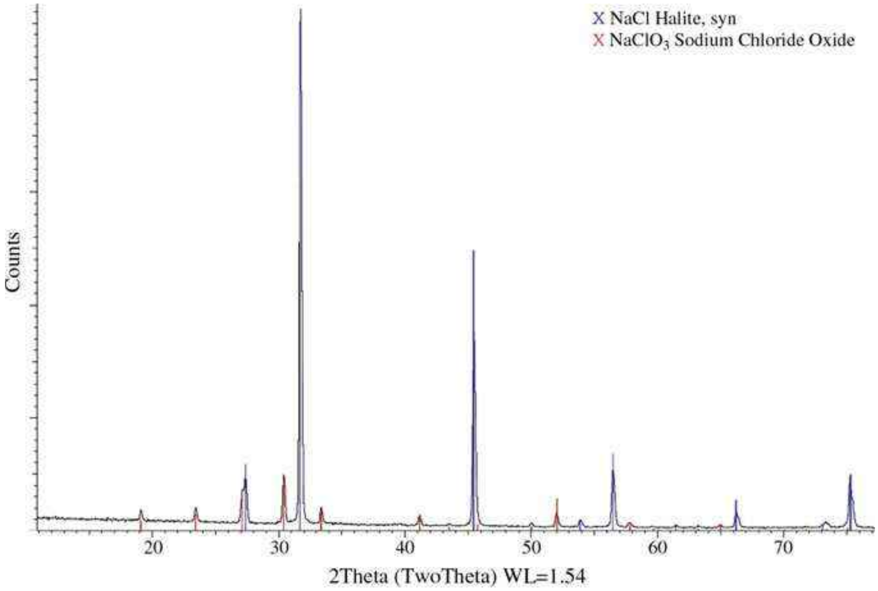


Fig. 10.20 X-ray diffraction pattern of post-reaction products from a mixture of bleach and molasses, primarily showing bleach, since sugars post-burning will not diffract

A forensic examiner performing fire debris and explosive analyses needs to be aware of the wide variety of starting chemicals and the potential resulting reaction products for **thermite**, **hypergolic mixtures**, and **chemical reaction devices**. Findings will vary, depending on the laboratory's available analytical techniques and what can be identified. Instrumental methods that provide an identification of compounds, as opposed to ions or elements only, are preferable, especially for these types of materials, since ions or elements alone may not be able to provide information on the original configuration of the compound. For example, identification of nitrate, chloride, potassium and sodium ions or elements does not delineate between an initial mixture of sodium nitrate and potassium chloride or an initial mixture of potassium nitrate and sodium chloride.

10.4 "Other" Fire Debris and Explosive Cases

The cases that fall into the "other" classification include those that may simply involve an explosive device (e.g., pyrotechnic aerial shell) attached to a Molotov Cocktail, a sample of explosive powder (e.g., smokeless powder) mixed with an ignitable liquid, and general unknowns, where investigators may not know if an explosion or fire occurred. For intact cases, where liquid and/or powder samples are present, analyses can be done in an order that preserves the most sample for further examination. Choosing techniques that are sensitive, selective, and non-destructive will ensure that sufficient sample remains to fully characterize the material.

In all post-fire/post-explosion instances where the potential exists for ignitable liquids, if the evidence is packaged appropriately in vapor-tight containers, then fire debris analysis should be performed prior to any other examination. If a volatile high explosive is also suspected, it is recommended to do headspace concentration for explosives at ambient temperature first, so as not to lose some of the thermally labile explosives, like TATP, HMTD, NG, and EGDN, or detection agents, like DMDNB. A follow-up headspace extraction at an elevated temperature or solvent extraction of selected areas can then be done to remove any ignitable liquids. For items that are not in vapor-tight packaging, the fire debris examination may not be possible, depending on laboratory policy.

Generally, a true unknown fire/explosion case will require examiner expertise and training to be able to evaluate the evidence submitted and the damage to the items to determine the proper analytical approach. For example, most explosive incidents involve a device of some type. Examination of the potential device components for blast damage and residue is key to deciding how to proceed with the analysis. When residue is observed, elemental or spectroscopic techniques could indicate an explosive profile, if one was present. Sometimes, components are not readily observed in masses of melted fire debris, and an X-ray of the material may be necessary to ascertain its contents. Examiners should exercise caution in interpreting results from fire/explosion scenes where no device components are present (or submitted) and extractions only identify ions. Environmental sources of the ions must be considered, especially where there is no evidence of explosive damage or potential device fragments. For example, nitrates are ubiquitous, commonly found in fertilizers, in latex and nitrile gloves as a coagulant, and in wastewater treatment. While nitrates are also common to many explosive compositions, a finding of this alone should be viewed cautiously.

10.5 Reporting

Ideally, one report would be issued for cases that involved both fire debris and explosive analyses. This, of course, requires that an examiner be qualified to write and testify to both. Having one report to explain the chemistry results is easier for the customer to read and understand. However, this is not always possible, due to laboratory policy, laboratory information management systems (LIMSs), or examiners not having completed competency testing in both of these disciplines.

One of the best examples to illustrate this point is for **ANFO**. In laboratories requiring two separate reports, the explosive report would state:

> Ammonium nitrate was identified.

The fire debris report would state:

> A heavy petroleum distillate (HPD) was identified. Examples of HPDs include diesel fuel and fuel oil.

But which report would relate these two for the customer to show that **ANFO** was present? If a single report was issued, then the following wording might be used:

> Ammonium nitrate and a heavy petroleum distillate (HPD) were identified. Examples of HPDs include diesel fuel and fuel oil. A mixture of ammonium nitrate and an HPD is also known as ANFO.

Alternatively, if two separate reports are written, one report could refer to the other, but the timing of the reports should be coordinated. For example, the fire debris report is issued first, and then the explosive report is issued with the following statement:

> Ammonium nitrate was identified. The fire debris report issued on Month/Day/Year identified a heavy petroleum distillate. A mixture of ammonium nitrate and a heavy petroleum distillate is also known as ANFO.

The advantage of having one report is that the customer is provided the result and conclusion at the same time, without having to piece together information from multiple separate reports. While most fire debris and explosive cases would benefit from having a single report, not every investigation needs this. **ANFO** and other similar mixtures are unique in that the combination of the oxidizer (e.g., ammonium nitrate) and the fuel (ignitable liquid) makes an explosive. Reporting these two individually, without making a link between them, could be misleading and uninformative to the customer.

10.6 Questions

1. Define a cross-disciplinary case as it relates to the information provided in this chapter.
2. Name at least one explosive mixture that contains a solid oxidizer and an ignitable liquid fuel.
3. What are incendiary mixtures?
4. What is a hypergolic mixture? Provide two examples.
5. Data for your case identifies sulfate ions, chlorate ions, and sucrose. A pH test of the residues indicated the presence of an acid. How would you report this?
6. You receive evidence packaged in a vapor-tight metal gallon can. The investigators do not know if a fire caused the explosion or an explosion produced the fire. How would you proceed with the analysis of the material in the can?

7. Evidence you receive contains white clumpy residues that were recovered after a fire. You identify potassium chloride and strontium carbonate. What are these compounds indicative of?
8. What is an advantage to identifying compounds instead of just anions and cations?

References

1. Defense Intelligence Agency (2012) Homemade explosives. Washington, DC
2. ASTM E1618-14 (2014)Standard test method for ignitable liquid residues in extracts from fire debris samples by gas chromatography-mass spectrometry. ASTM International, West Conshohocken, PA, www.astm.org
3. Reardon MR, Bender EC (2005) Differentiation of composition C-4 based on the analysis of the process oil. J Forensic Sci 50:564–570
4. Reardon MR, Allen L, Bender EC et al (2007) Comparison of motor oils using high-temperature gas chromatography-mass spectrometry. J Forensic Sci 52:656–663
5. Hibbard R, Goodpaster JV, Evans MR (2011) Factors affecting the forensic examination of automotive lubricating oils. J Forensic Sci 56:741–753
6. Brumley WC, Jones WJ, Grange AH (1995) A survey of potential applications of high-temperature capillary gas chromatography for environmental analysis. LC GC 13:228–236
7. Buyten J, Duvekot J, Peene J, Musschee Ph (1991) A capillary column for hightemperature gas chromatography. Am Lab 13:8
8. Roehner RM, Fletcher JV, Hanson FV (2002) Comparative compositional study of crude oil solids from the trans Alaska pipeline system using high-temperature gas chromatography. Energy Fuels 16:211–217
9. Chakraborty A, Bagchi S, Lahiri SC (2015) Studies of fire debris from bomb blasts using ion chromatography, gas chromatography-mass spectrometry and fluorescence measurements—evidence of ammonium nitrate, wax-based explosives and identification of a biomarker. Aus J Forensic Sci 47:83–94
10. Reardon MR, Proudfoot JE (2007) Oils and waxes in composition C-4 and emulsions: a comparison of intact samples to post-blast residues. In: Proceedings of the 9th international symposium on the analysis and detection of explosives, Paris, July 5, 2007
11. Beveridge A (ed) (2012) Forensic investigation of explosions. CRC Press, Boca Raton
12. Conkling JA, Mocella CJ (2011) Chemistry of pyrotechnics. CRC Press, Boca Raton, FL
13. Arsenal Picatinny (1974) Encyclopedia of explosives and related items. Dover, Mineola
14. Dean WL (1984) Examination of fire debris for flare (fusee) residues by energy dispersive X-ray spectrometry. In: Proceedings of the international association of forensic sciences, Oxford, 1984
15. Nesvold S, Pacholke K (2012) Detecting and confirming the presence of road flare residue in fire investigations. In: Proceedings of the 5th international symposium on fire investigation science and technology. National Association of Fire Investigators, International, Sarasota, 2012
16. Stauffer E, Dolan JA, Newman R (2008) Fire debris analysis. Academic Press, Cambridge
17. Kirkbride KP, Kobus HJ (1991) The explosive reaction between swimming pool chlorine and brake fluid. J Forensic Sci 36(3):902–907
18. Martin-Alberca C, Ferrando JL, Garcia-Ruiz C (2013) Anionic markers for the forensic identification of chemical ignition Molotov Cocktail composition. Sci Jus 53:49–54

19. Hutches K, Lord J (2012) A new kind of Molotov? Gasoline-pool chlorinator mixtures. J Forensic Sci 57:1064–1069
20. Centers for Disease Control and Prevention (2003) Homemade chemical bomb events and resulting injuries—selected states, January 1996-March 2003. MMWR 52:662–664
21. Centers for Disease Control and Prevention (2013) Homemade chemical bomb incidents—15 states, 2003–2011. MMWR 62:498–500
22. Wade D (2013) Ignition devices for prescribed burning. http://southernfireexchange.org/SFE_Publications/factsheets/2013_3.pdf. Accessed 20 Mar 2018
23. SEI Industries (2017) Fire ignition sphere. http://www.sei-ind.com/products/fire-ignition-spheres. Accessed 20 Mar 2018
24. Beveridge AD, Greenlay WRA, Shaddick RC (1983) Identfication of reaction products in residues from explosives. In: Proceedings of the international symposium on the analysis and detection of explosives, Quantico, 29–31 Mar 1983
25. Nowicki J, Pauling S (1988) Identification of sugars in explosive residues by gas chromatography-mass spectrometry. J Forensic Sci 33:1254–1261
26. McDonald K, Shaw M (2005) Identification of household chemicals used in small bombs via analysis of residual materials. Paper presented at the 57th annual meeting of the American Academy of Forensic Sciences, New Orleans, Feb 2005

Michelle Evans has worked as Forensic Chemist for the Bureau of Alcohol, Tobacco, Firearms and Explosives Forensic Science Laboratory since 2000. She earned a BS in chemistry from the College of William and Mary and a MS in forensic science from the George Washington University. As ATF Chemist, she analyzes evidence related to explosive and fire investigations, assists at scenes, instructs law enforcement personnel on a variety of laboratory topics, and publishes research related to both explosives and fire debris analysis.

Chapter 11
Interacting with Other Disciplines

Carl E. Chasteen

Learning Objectives

- Understand the nexus between fire debris and explosives analysis and other forensic disciplines.
- Understand the effect fire and explosion may have on evidence collected for forensic disciplines other than fire debris or explosives analysis.
- Understand how the application of common fire debris or explosives analysis methods can affect a sample and its suitability for other forensic tests.
- Understand the proper methods to divide or sub-select portions of samples to increase the number of forensic disciplines that may be applied.
- Understand the application of the 'best evidence' principle when a choice of forensic disciplines must be made because of sample limitations.

Evidence from a fire or explosion investigation will often require more than simply a fire debris or explosive analysis. While fire debris and explosives examinations provide important information about what happened, they generally cannot provide information about who caused it to happen. The following sections provide additional information that will assist the fire debris or explosives examiner to understand how other examinations will affect their evidence and what they can do to ensure that other examinations remain viable.

A forensic laboratory must have a plan in place to determine the order and manner in which evidence is approached to ensure full exploitation of the evidence. A determination of whether other forensic examinations will be needed for a given set of evidence should be made before the fire debris or explosives examiner begins interacting with the evidence. Each step of the examination process (sample

---

C. E. Chasteen (✉)
Division of Investigative and Forensic Services, Department of Financial Services,
Bureau of Forensic Services, Havana, FL, USA
e-mail: carl.chasteen@myfloridacfo.com

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4_11

preparation, extraction, storage, etc.) could significantly impact the outcome of other disciplines of forensic testing. It may be necessary for the examiner to determine not only the order of the testing, but whether sub-sampling may be required so that the broadest variety of forensic disciplines can be applied.

11.1 Forensic Biology and DNA Testing

Jason R. Bundy, Forensic Quality Manager, Florida Dept. of Law Enforcement, Tampa Regional Laboratory.

Forensic biology is primarily concerned with linking an individual (suspect or victim) to or eliminating them from a crime scene or a piece of evidence through **DNA analysis**. As DNA techniques have developed over time, DNA analysis has become one of the most powerful tools in forensic science. The great advantage of DNA analysis is the ability to link a specific person to an item or a location. However, it cannot tell you how or when the DNA came to be at that location or why it is there. Furthermore, with increasingly sensitive methods, the potential for contamination of DNA samples has increased. Forensic biology also includes body fluid identification, or serology, which may be used to locate potential DNA sources on large items and confirm the expected biological source of the DNA profile (i.e., semen or blood). However, serological screening has become significantly less useful in court compared to the comparison of DNA profiles due to the highly sensitive and specific results one can obtain from DNA testing.

11.1.1 The Basics of DNA Analysis

Forensic DNA testing uses individually varying lengths of DNA in several specific regions, or loci, that together make up a ‘profile’ of DNA in a method called short tandem repeat (STR) DNA analysis. A DNA profile is comprised of the determined lengths of DNA at each locus. Due to the variability in lengths of DNA at each locus within the general population, this type of testing is capable of assigning a high statistical weight when an individual’s DNA profile is linked to a DNA profile recovered from a piece of evidence.

Frequently, none of the areas tested on a given piece of evidence are able to provide a full DNA profile, reducing the strength of the comparison. The two common reasons this occurs are the degradation of DNA and the inhibition of the chemical processes to complete the analysis. Degradation of DNA is the process of breaking the bonds that hold DNA together. A few breaks will have little effect on DNA analysis, but many breaks may cause the DNA analysis to return no usable profiles [1]. While technology has significantly improved and increased the profiles suitable for comparison from degraded DNA by using shorter ‘mini-STRs’, it only works for lightly degraded samples. Many of the DNA testing processes use varying pH, temperature, or salt concentrations to work, so any chemical that is known to alter these characteristics may inhibit the efficiency of the STR DNA testing.

DNA collected from a crime scene comes in various forms and amounts, including biological fluids, skin cells, tissue, and bone. A large amount of viable DNA may be present in a bloodstain (depending on its exposure to heat) while little DNA may be present on a broken Molotov cocktail, where the chemical or ignitable liquid contents have impinged on the areas where DNA was originally present. While the ignitable liquid may not degrade the DNA, it may interfere with the processing of the DNA. In crime scenes with fire or explosion damage, DNA may be extremely limited, particularly when the majority of the scene has been burned or impacted by a pressure wave. Evidence originally collected for fire debris or explosives analysis may also have areas or portions that are appropriate for DNA analysis. This is where the examiner must exercise their knowledge of the requirements of other forensic disciplines to ensure full exploitation of the evidence.

11.1.2 DNA in Samples from Fire or Explosion Scenes

Locating DNA at a fire or explosion scene or on collected items can be complicated. In a fire scene, soot and water may have covered the areas of interest, potentially concealing and diluting any biological fluid. Fire suppression and overhaul activities may also wash away fluids and deposited cells and may remove potential evidence from where it was originally located. Overhaul sometimes removes materials from a scene to a pile of material outside of the structure to eliminate the potential for the fire re-kindling.

In an explosion, the pressure wave may have scattered the materials with potential DNA. People investigating bombing scenes often swab witness materials, as discussed in Chap. 8. If there was a human victim who had body materials removed and scattered by the explosion, it is possible that the swabs may capture some of their cells or biological fluids, which can be tested for the presence of DNA. Unfortunately, explosives analysis will typically consume these swabs, so it is important for examiners and investigators to communicate as to which examination is more pertinent for the investigation.

Evidence collected for fire debris analysis may also contain potential DNA. Containers used to transport an ignitable liquid to the scene by a perpetrator, such as gasoline cans, may have some DNA present in deposited skin cells. Cloth used to make wicks for Molotov cocktails may have biological fluids or skin cells, particularly if they are fashioned from clothing. In some cases, the perpetrator may use a delay device that uses a lit cigarette, which can potentially contain DNA from initial ignition of the cigarette. In addition, if the perpetrator is a smoker, there will often be cigarette butts left outside or inside the scene. The original investigator may not be aware that these items could possibly be tested for DNA and may initially only submit them for ignitable liquid analysis because they appear to be part of an incendiary device. The fire debris/explosives examiner should be cognizant of the potential for these examinations and discuss them with the investigator.

Areas in a fire with higher temperatures typically have recovery of fewer DNA profiles [2]. The time and intensity of the fire will greatly impact the extent to which DNA may still be intact within the crime scene. Bloodstains are a visually obvious potential source of DNA in a scene with fire damage. The use of chemicals which may reveal the presence of blood (such as Luminol® or Blue Star®) or an alternate light source which can help with detection of bodily fluids may be useful in finding some of these sources. The use of visualization agents such as Blue Star® and Luminol®, which are used to find bloodstains and residues, will not deleteriously affect the DNA [2]. However, like any items used to assist in collecting evidence, a comparison sample of the visualizing agent should be submitted to determine any interference with ignitable liquid analysis. The soot coating the blood spatter may have to be washed off with water before the blood detection chemicals will be effective. Unfortunately, blood spatter covered by soot may have been exposed to heat at a level, which would degrade the DNA. Knowledge of fire behavior and dynamics indicates that the spatter or other sources of DNA found closest to the floor or farther away from the point of origin have likely been exposed to lower temperatures (depending on the other fire dynamics parameters). If there are human remains such as bone and tissue from an unidentified individual found in the scene, these may be submitted for DNA testing for identification purposes.

DNA sources that are not visible may also be present at crime scenes. This poses an obvious challenge for collection. Touch or trace DNA is DNA, typically skin cells, that is deposited from contact with a surface or item. Touch DNA typically leaves very small amounts of DNA, though increased sensitivity of analytical methods allows for the development of a useable DNA profile in many cases. The amount of touch DNA left on a surface or item varies based on a variety of factors including the duration and intensity of contact from a donor and the nature of the item; a single contact may not produce a DNA profile even in ideal circumstances. As with other sources of DNA, touch DNA can be degraded by exposure to environmental conditions [3]. In fire- or explosion-related crime scenes, touch DNA may be difficult to isolate on a sample due to the limited amount of DNA left behind, the direct effects of a fire/explosion, and the effect of subsequent fire suppression activities (water, foam, etc.). Despite these considerations, touch DNA can be a very valuable source of evidence and attempts at recovery should be made. Any item or surface that a perpetrator may have handled or touched may be a source of touch DNA including door handles, tools used to break into a scene, gasoline containers, and explosive or incendiary device components (bottles, metal or plastic pipes, wires, etc.).

11.1.3 Packaging Considerations for DNA Evidence

The general collection and storage of DNA have certain requirements that must be followed to ensure that the evidence is not compromised further than it is when found at the scene. Most commonly, a sample is collected from a dried stain of blood or the evidence is swabbed using a sterile swab with sterile water. These swabs are then dried, packaged, and labeled to prevent cross-contamination or misidentification later. DNA evidence can generally be stored dry at room temperature, refrigerated short-term if it is a biological fluid (liquid), or frozen. If no ignitable liquid analysis is required, DNA evidence stored at room temperature should be in paper or another breathable packaging to avoid the accumulation of moisture that occurs if sealed in plastic. Plastic containers can be used for refrigerated or frozen samples to ensure no liquid will seep into and through the outside container, potentially contaminating another piece of evidence. Moisture is the biggest hazard to DNA prior to being tested. This is due to the bacteria present in moisture that can very quickly degrade DNA [1].

Any evidence to be tested for ignitable liquids must be packaged in vapor-tight packaging, which is in direct conflict with preferred packaging for DNA analysis. If an item of evidence is not packaged in vapor-tight packaging, no ignitable liquid analysis should be performed. On the other hand, if an item is packaged in vapor-tight packaging, DNA analysis can still be performed. Generally, passive headspace concentration (PHC) should be performed before DNA analysis because it is relatively noninvasive to the sample (see Chap. 2). Solvent extraction should be avoided; if it is absolutely necessary, it should be conducted carefully to try to preserve as much of the sample for DNA analysis as possible. Upon completion of the fire debris analysis, the sample can be laid out to dry or (depending on laboratory protocols and the other tests to which it is to be subjected) repackaged for DNA analysis as soon as possible to maximize the evidentiary value. Alternative options for items that require fire debris and DNA analysis may be to freeze an item to preserve the sample, or separate a sub-sample for each analysis. For example, a portion of the sample, such as a visibly bloodstained region, can be collected for DNA and the remainder sent for testing for ignitable liquids. In most situations, however, ignitable liquid analysis should occur first.

There are generally fewer issues in coupling DNA and explosives analysis, but where vapor-tight packaging is used for explosives evidence, the same considerations apply as discussed for fire debris.

There may be scenarios where either the DNA or fire debris/explosive examination must be prioritized over the other, depending on the needs of the case and throughput concerns. In these cases, the best approach is to identify the need for DNA and IL testing from the beginning. The investigator should submit the sample to the laboratory as quickly as possible, and then, the examiner can immediately do a passive headspace extraction. Once the extraction is complete, the sample can be sent for DNA analysis. Depending on the environment, DNA is stable at temperatures below 100 °C, with complete degradation occurring around 190 °C [4].

Temperatures routinely used in headspace extraction (approximately 60–65 °C overnight) will not degrade the DNA, no freezing/thawing of sample is necessary, and exposure of DNA to a moist environment is limited. In other cases, the presence of an ignitable liquid may be proven by other methods (video evidence, for example), and the more important evidence is the DNA profile of whoever brought the ignitable liquid onto the scene. In these types of cases, the fire debris analysis can be canceled in favor of quickly processing the DNA analysis. Again, communication between disciplines and the submitter is useful for determining what testing is needed for the evidence.

Anytime that DNA testing is considered, the strict adherence to wearing gloves and masks and reducing the personnel handling the evidence is critical to ensure there is no contamination of the evidence. With the sensitivity of modern DNA techniques, there is much greater risk for contamination. For example, gloves that have been worn to open evidence packaging should be changed prior to touching the actual item of evidence as secondary DNA transfer may occur, transferring DNA from the exterior packaging to the evidence via the examiner's gloves. Reducing the likelihood of extraneous DNA sources can be the difference between a profile suitable for comparison and a complex mixture of low-level DNA information. If DNA at the scene has been compromised by multiple contributors, the likelihood of results with little to no value will also increase. Accounting for these exogenous contributors requires the collection of swabs from all first responders or others who may have contacted the evidence for elimination purposes.

Current forensic methods and test kits for DNA are more sensitive than previous iterations and can give results for more degraded evidence than ever before. By careful handling, reduction of handling, and drying collected samples once ignitable liquid testing is complete, DNA testing should be viable even when additional testing is required for other disciplines such as fire debris or explosive analysis.

11.2 Toolmark Analysis

Ron Nichols, Nichols Forensic Science Consulting.

In toolmark identification, a **tool** is defined as an implement to gain a mechanical advantage. It is also commonly thought of as being the harder of two objects such that when it comes into forcible contact with another, softer, object, it will leave a mark on that object. That mark is referred to as a **toolmark**.

Toolmark identification is a discipline of forensic science that primarily seeks to determine whether a toolmark was produced by a particular tool. The presence of toolmarks on fragments from improvised explosive devices is quite common because tools are often used in the construction of the parent devices. Less common, but of consideration, is the presence of toolmarks on doors, windows, cabinets, safes, or other locks that have been forced open to gain access. In addition to determining whether a toolmark was produced by a particular tool, trained toolmark examiners can evaluate observed toolmarks and potentially determine the type of tool used to produce the toolmark along with more specific features on the tool surface. This can be valuable information for investigators looking to secure a search warrant or provide them guidance in determining which tools of a well-stocked workshop should be confiscated. Trained toolmark examiners can also intercompare toolmarks in the absence of a tool in an effort to determine whether the same or multiple tools may have been used in the construction of a device or the forcing of a locked object. In one particular case, toolmarks on recovered electrical components from an exploded device were compared with toolmarks on similar components of an unexploded device known to have been constructed by a particular individual. Even though the tool was not available for comparison, the knowledge that the same tool generated those toolmarks on each of the devices helped provide the link the investigators needed.

11.2.1 Types of Toolmarks

In general, there are two types of toolmarks that may be observed. One is an **impressed mark**, which occurs when a tool surface contacts an object with sufficient force to leave behind an impression of that tool surface in that object. Figure 11.1 illustrates an example of impressed marks. The second type of mark that may be observed is a **striated mark**, which appears as a series of microscopic scratches on the surface of an object. This type of mark is generated when a tool is in contact with an object and then moves across the surface of that object, scratching the surface and leaving behind these microscopic lines or striations. Figure 11.2 illustrates an example of striated marks caused by the slipping of teeth from pliers as the pliers were rotated around the copper fitting. At times, there can be a combination of both when the tool is compressed into an object and then slips along the surface of that object, such that the striated mark emanates away from the impressed mark.

These toolmarks are very useful in that the combination of features within the toolmark can be used to link the toolmark to the tool that created it. These features include what has been commonly referred to in the toolmark discipline as class and individual characteristics. **Class characteristics** are measurable features common to a particular group of objects, typically intended and produced by design. For example, slotted screwdrivers with a flat edge are designed with an intended purpose and will have different blade dimensions commensurate with that purpose. Another example would be slip joint pliers with serrated jaws. The width of each jaw is a class characteristic as is the spacing of the teeth along the surface of each jaw as depicted in Fig. 11.3. Often, class characteristics can be assessed to aid the investigator in determining the type of tool that was used in the creation of a particular toolmark. For example, in Fig. 11.5 the piece of wire (b) has a profile in which two angled surfaces come together at a point. Such a profile is caused by a

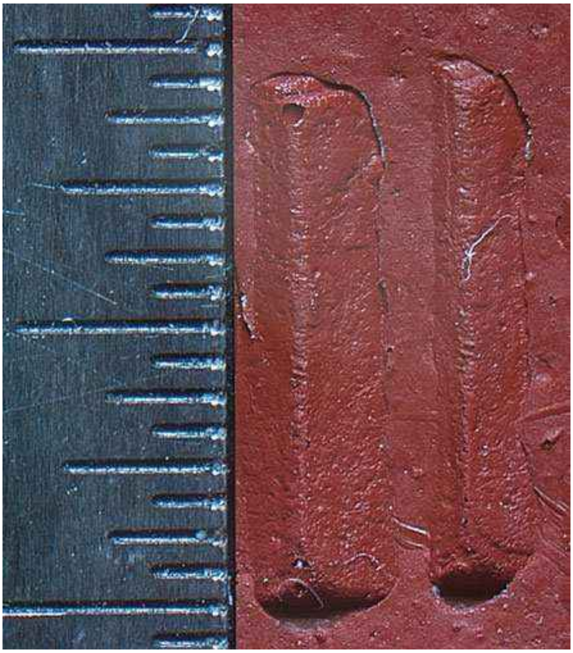


Fig. 11.1 Cast of impressed toolmarks produced by adjacent teeth from the jaw of a wrench. There is no lateral movement of the tool with the surface

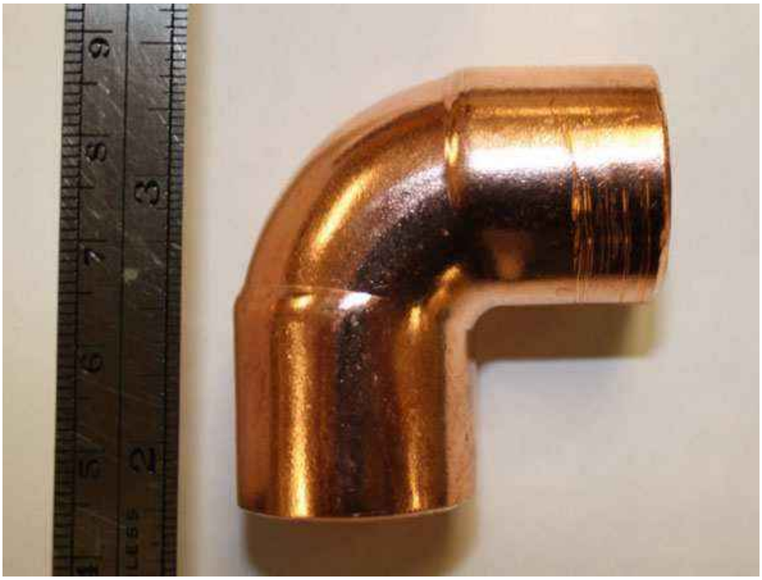


Fig. 11.2 Striated toolmarks caused by the movement of the teeth of pliers as the jaws gripped the pipe fitting and were rotated around it

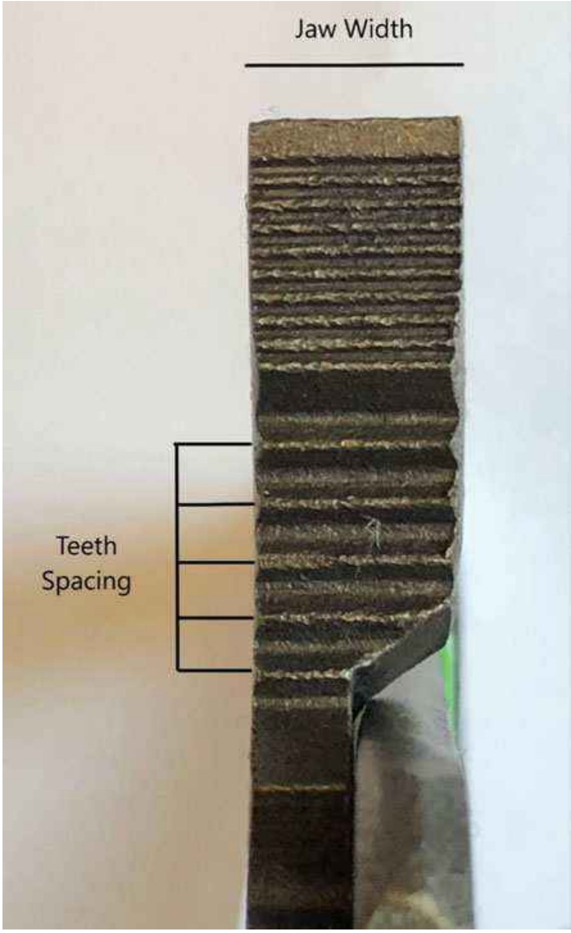


Fig. 11.3 A single jaw from slip joint pliers illustrating two class characteristics—jaw width and spacing of the teeth on the jaw

tool having a double-edged cutter (a) in which the blades cut into each side of the wire, and as they come together, the wire is pinched by the two blades and breaks.

11.2.2 Individualizing Toolmarks

Individual characteristics are random imperfections and irregularities on the working surface of the tool created incidental to the manufacturing process of that tool. That means that they are unintended and not a design feature, simply a consequence of the manufacturing process of that tool surface along with, potentially, later use. These marks can be microscopic or observable to the unaided eye, such as might happen if a tool surface breaks. The combination of such

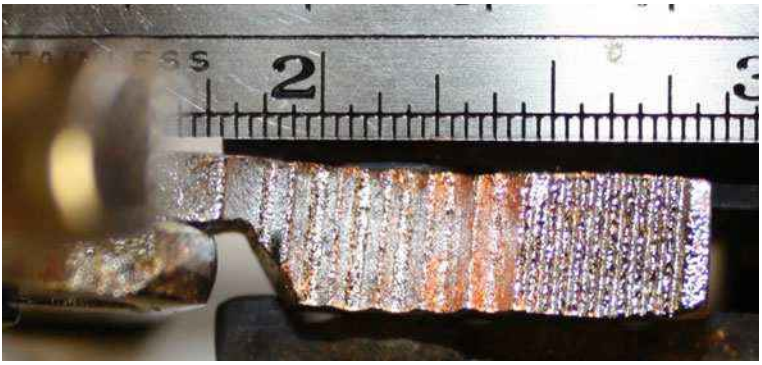


Fig. 11.4 Jaw of pliers with trace copper residues on the surface of the teeth. During the examination of tools, it is important to evaluate tool surfaces for such trace evidence, which can provide information about the use of that tool

characteristics on a tool surface is generally considered unique to that tool and can be used to differentiate that tool from others having similar class characteristics. It is also important when assessing the tools suspected of being the source of the toolmark to consider if there may be trace evidence present, which needs additional testing as depicted in Fig. 11.4.

11.2.3 Toolmarks from Fire or Explosion Scenes

For fire debris and explosive examiners, the consideration is whether any of these items which may have toolmarks present have been adversely affected by the fire or explosion. Pressure may deform the toolmark and potentially tools left in or near the scene. Should either be deformed, it can cause the resulting examination to be significantly more challenging. However, the issue of deformation may not be discernable to the fire debris or explosive examiner and should be taken to the toolmark examiner for their judgment. The collection and preservation of evidence from a fire or explosion often require the evidence to be packaged in an airtight container. Depending on the laboratory, it may be days, weeks, or even months before the item is opened and examined. A ferrous item sealed in a container with even a small amount of moisture may rust on the surface, thus rendering the item useless to the toolmark examiner if the toolmark or tool surface is rusted. Other materials, composed of organic materials such as wood or plastic door or window frames and flooring that have an impression from a tool on them, may allow the growth of mold in the sealed container, which might render them useless as well. If a fire debris or explosives examiner determines that there is a potential for the evidence item or a portion of it to be useful for toolmark examination, the examiner should coordinate with a toolmark examiner to determine if the item should be dried.

11.2.4 Conclusions from Toolmark Analyses

When making toolmark comparisons, examiners generally will reach one of several conclusions. The first is an identification, in which class characteristics agree and there is sufficient correspondence of individual markings to support that the toolmarks were created by the same tool. It should be noted that when offering such an opinion, the examiner is not implying that such a determination is made to the exclusion of all other tools. The AFTE Theory of Identification, a consensus statement of the Association of Firearm and Toolmark Examiners (AFTE), discusses a practical identity. This means that while not every tool can be examined, the likelihood of another tool producing that toolmark is so remote that for all practical purposes it can be ignored. The second conclusion that may be reached is an exclusion, in which class characteristics are different or there is a significant difference in individual characteristics in the toolmarks. The third conclusion that can be reached is referred to as an inconclusive, an opinion typically rendered when class characteristics agree, but there is insufficient correspondence for an identification or insufficient differences for an elimination. The last conclusion that may be offered is that the toolmark is unsuitable for comparison or identification. This would also be the likely conclusion if fire or explosion had deformed either the tool or the surface markings to which it was to be compared.

Figure 11.5 illustrates a case example in which assessments, examinations, and comparisons have been made leading to the identification of some toolmarks with a submitted tool and the elimination of other toolmarks as having been made by that tool. The submitted tool is a double-edge wire cutter, often referred to as a side cutter because of the blade design (a). Using the submitted tool and wire similar to the wire in question, test marks were produced in that wire resulting in the profile represented in (b). This profile is different from the profile observed on one of the evidence wires (c) and thus serves as the basis for an elimination based on different class characteristics. When compared with other submitted evidence toolmarks as illustrated in (d), there was sufficient correspondence of a combination of individual markings to conclude that the submitted tool did produce the other toolmarks present on submitted evidence.

For the most part, fire debris or explosives analysis will not interfere with toolmark examinations. During their examination, the fire debris and explosives examiner should note the presence of any wiring, pipes, tubes, or other items in the submitted exhibit. If noted, these may need to be sent to the toolmark examiner for a proper evaluation and potential comparison with submitted tools.

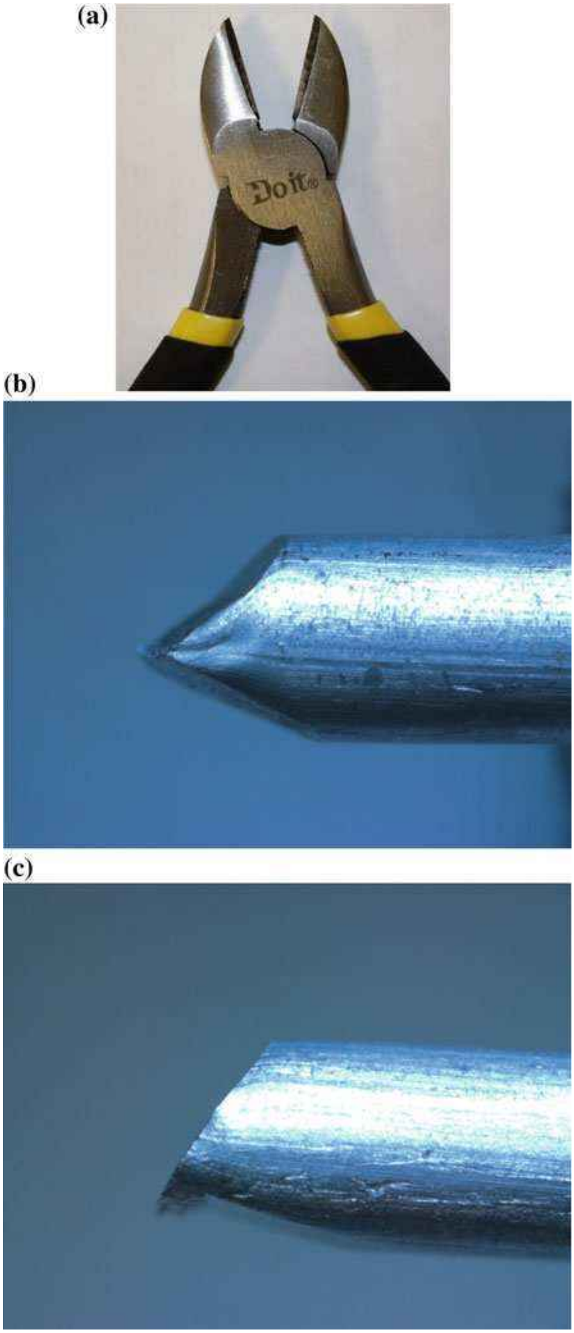


Fig. 11.5 **a** In this case example, the submitted tool is a double-edge wire cutter, often referred to as a side cutter because of the blade design. **b** Test marks were produced in that wire resulting in a profile representative of a double-bladed cutter. **c** Profile in **b** is different than what is seen on **c** and thus serves as the basis for an elimination based on different class characteristics. **d** Toolmarks in comparisons

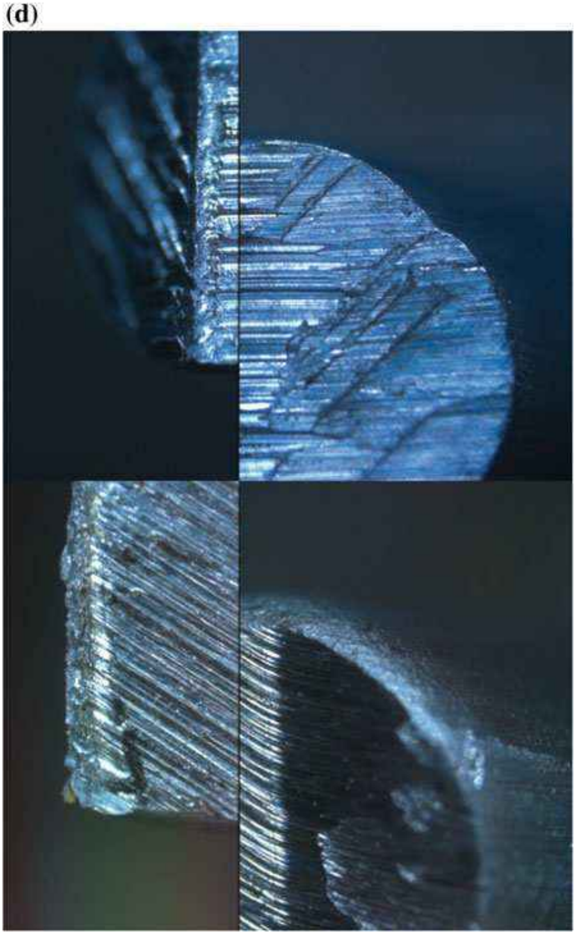


Fig. 11.5 (continued)

11.3 Latent Print Evidence

Tania Kapila, Fingerprint Specialist, Bureau of Alcohol, Tobacco, Firearms, & Explosives, Forensic Science Laboratory-San Francisco.

Friction ridge skin is present on the palm (palmar) side of the hands and the soles (plantar) of the feet. It has a corrugated appearance, with the ridges being higher than the furrows. In order for a latent print to be created, there must be a matrix; when referring to latent prints, a **matrix** is a substance deposited on the friction ridge skin and the surface on which the print will be deposited. This matrix can be blood, paint, dust or dirt, oil, etc. Natural secretions from the eccrine glands (sweat) and sebaceous glands (oils) are made by the human body, so these are probably the most common matrices in latent prints [5]. The term 'latent' is Latin for hidden or unseen; however, in forensic science, the term is often used generically for any reproduction of a friction ridge skin pattern recovered from an item of evidence or crime scene, whether visible or the result of chemical enhancement. It is important to remember that latent prints produced with sweat are almost 99% water, which means they can be very fragile [6]. As such, care in handling any object suspected to have latent prints is important.

11.3.1 Factors Affecting the Recovery of Latent Prints

By the nature of their chemical composition, latent prints are particularly susceptible to damage. The damage may be the result of environmental conditions, such as high temperatures, or excessive friction, and rough treatment resulting from the initial event and subsequent suppression, overhaul, or rescue operations. After sufficient exposure to heat, latent prints may lose their original water content; however, residual solids from the print, such as salts, may still be present and useful for latent print development [7]. Alternatively, fire suppression techniques such as water from a fire hose and chemical fire extinguishers can wash away latent print residues or damage them to the point that they are no longer of value for identification purposes.

The initial event can have further effects on the recoverability of latent prints beyond simply the heat-related degradation. For example, in an explosion, items close to the blast seat, e.g., parts of a device, are moved rapidly by the force of the explosion's pressure wave, and they may drag or tumble along the ground. The friction from dragging and tumbling can potentially wipe latent prints from the surface. In a fire, items that are more distant from the flames may not be exposed to excessive heat, but soot can build up on the item and be difficult to remove. There have, however, been studies conducted that demonstrate that removal of soot can reveal identifiable latent prints [8]. As such, it is important to handle post-fire and post-explosion evidence carefully, even if it seems initially as though there is little likelihood of latent prints being present.

Ultimately, at a fire or explosion event, the first priority on scene is safety and fire suppression. First-responding personnel are not necessarily considering evidentiary value as much as they are attempting to rescue victims and mitigate hazards. Items may not be able to be protected from accidental damage from falling debris, shoveling, and other rough handling or moving of objects during this initial phase. Regardless of the challenges posed by these types of scenes, viable latent print evidence may exist.

11.3.2 Handling of Evidence

It is important to think about how to handle the evidence prior to fingerprint examination. Improper or excessive handling of evidentiary items probably destroys more latent print evidence than any other factor.

A fire debris or explosive chemist ideally receives the evidence early in the laboratory processing scheme. It is the responsibility of the chemist to handle the evidence carefully so as not to damage any latent prints present during the course of their analysis. There are several factors to consider, such as:

- Is the item porous or non-porous? Porous items absorb the residue from the latent prints and therefore provide a form of protection from being easily wiped away. Latent prints on non-porous items, on the other hand, are on the surface of the item, making them extremely fragile and more susceptible to damage.
- Is the item smooth or textured? Smoother surfaces are better for developing an identifiable latent print as there is less chance of interference between the skin and the surface. As the surface becomes more textured, the skin's ability to make full contact with the surface decreases. As contact between the friction ridge skin and the textured surface decreases, the possibility of developing a usable latent print decreases. There are various techniques that aid in visualizing latent prints on some textured surfaces; therefore, a latent print examiner should be consulted prior to handling this type of evidence. Keep in mind that textured surfaces are good for DNA evidence, and when possible should be swabbed prior to a latent print examination.
- What is the size of the item? The smaller the item, the less surface area there is to leave a latent print on. The smaller the latent print gets, the less quantity of detail there is which can decrease the chances of the latent print being identifiable.

If the chemist does have to handle the item prior to the latent print examination, they should attempt to do so in a way that makes minimal contact and is different from normal handling. For example, if the item is a soda can, an index finger can be placed on the top rim and thumb on the bottom rim of the can (taking care to avoid the mouth area for possible DNA evidence). This type of handling attempts to avoid contact with the regions that are the most likely to yield viable latent print evidence.

No evidence should be handled without wearing gloves, but it should be noted that gloves do not protect the latent prints on the item from being damaged; they protect the examiner from exposure to contaminants and they may protect the examiner from leaving prints on the item, but not always. It is possible for latex gloves that get contaminated with dirt or other substances to transfer the examiner's fingerprints onto an item [9, 10].

11.3.3 Latent Print Processing

There are various ways to process an item of evidence for latent prints after a thorough visual examination. Each laboratory's policies and procedures should be consulted for specific details. A common technique that many laboratories use for processing non-porous items is cyanoacrylate fuming. Prior to fuming, the item is exposed to humidity in an attempt to rejuvenate the moisture that may have been lost in the latent print. Then, a small amount of cyanoacrylate is heated and the fumes polymerize on any latent print residue on the item. After the fuming process, it is possible that the latent prints are visible and can be photographed. The next step is usually to apply one of many dye stains, which adhere to the cyanoacrylate residue and will fluoresce when viewed with an alternate light source. At this point, any latent prints that are fluorescing can be photographed. Traditional powder processes can be used either before or after the dye stain process.

If an item is porous, there are several chemicals, such as ninhydrin, that can be used to make the latent prints visible. These chemicals can be applied by using a squirt bottle, spraying, brushing, or dipping the item. If the item will also be examined for DNA, it should not be brushed or dipped to prevent cross-contamination of loss of biological material that may be present. Semi-porous items, such as glossy cardboard, can go through both the non-porous and porous processes.

11.3.4 Fire Debris Evidence

It is important that a fire debris chemist starts with the evidence so that the latent print processing does not compromise their examination. The application of a dye stain or other chemical rinse may literally add a solvent (ignitable liquid) to the evidence, unavoidably contaminating it for future fire debris analysis. Additionally, the cyanoacrylate fuming of the evidence typically involves multiple items being exposed to air at the same time, risking cross-contamination of ignitable liquid residues. The evacuation of the fuming chamber that follows the fuming would potentially eliminate remaining ignitable liquid residues. The fire debris examination, however, should be performed in a way that maximizes the total useful evidence that can be obtained from the item. Discussion between examiners, where possible, is ideal to determine the best approach to the evidence.

Common items seen include glass bottles, gas cans, cloth, paper, cigarettes, matches/matchbooks, and lighters. The damage to items from a scene can range from practically free of soot/fire damage to heavily soot-/fire-damaged. The more damage to the item, the less chances of recovering identifiable latent prints; however, studies have reported that if the soot is deposited prior to the moisture in the print evaporating, it increases the likelihood that prints can be recovered [8]. Heavily damaged items may still have protected areas, areas that were protected

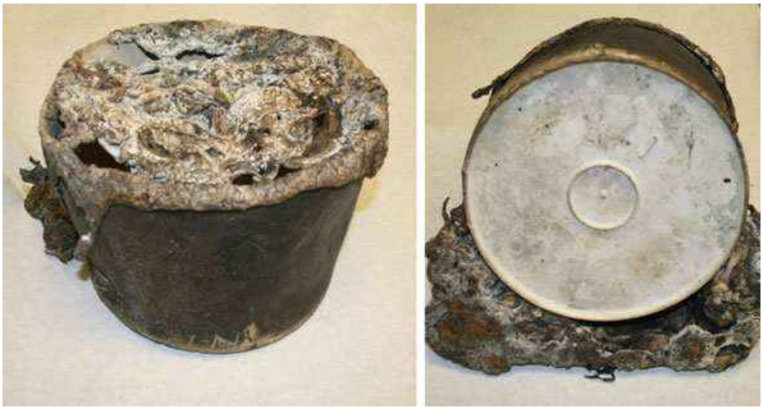


Fig. 11.6 Melted plastic container (left) with protected area on the bottom (right)

from the fire. The protected areas are still viable areas to develop latent prints (Fig. 11.6).

Fire debris evidence should be evaluated for DNA as well, particularly protected areas. Whether the item is swabbed prior to a latent print examination, after a latent print examination, or both will still depend on whether the surface is textured or smooth. For example, a lighter should have the textured wheel, which is not a good surface for fingerprints, swabbed for DNA prior to the latent print examination and the remaining areas swabbed after the latent print examination. The mouthpiece of bottles should be swabbed for DNA regardless of what the bottle contained prior to collection. Keep in mind that DNA can be recovered from the mouth area of bottles that contained other liquids that are not intended for consumption. Gasoline cans, and any container with a handle, should have the handle area swabbed. The normal handling areas, such as the neck of a bottle or bottom of a gas can (when pouring a full can it is normal to have one hand on the handle and one on the bottom for support), should be considered.

Ideally, cigarettes should be examined for latent prints first. When the cigarette only has a small filter area left, it may be sent to the DNA section without subjecting it to the chemical processes in a latent print examination, as this is likely the ‘best evidence’ for this small item. Paper can be swabbed or cuttings can be taken after a latent print examination. Depending on what chemical process was used, there may be areas on the paper where the reaction caused a color change, with or without visible friction ridge detail, which may indicate the presence of proteins, fats, or oils. These are good indications for areas to swab or cut for DNA analysis [11]. Cloth wicks may not suitable for a latent print examination, but good for a DNA examination. After the evidence has been processed for latent prints, there may be areas of ridge detail that can be swabbed (only after a latent print examiner has preserved necessary ridge detail). There may also be areas that indicate contact was made, such as areas that have what appear to be swipe marks of fingers even though there is no ridge detail present. These areas may also be good areas for DNA swabbing.

11.3.5 Explosives Evidence

As in fire debris analysis, it is important that an explosive chemist starts with the evidence, if possible, so that the latent print processing does not compromise their examination. Once again, different sections should work hand-in-hand to evaluate the evidence to see what examinations can be performed and in what order they should be conducted. For example, if tape is wrapped around a pipe, it is ideal for the explosives chemist to perform a rinse on the interior of the pipe prior to the latent print examiner processing the tape. This allows the explosives examiner to identify the post-blast residues (as discussed in Chap. 8) while retaining the potential latent prints on the pipe and tape exterior. The ends of the tape should be carefully preserved for comparison to any rolls of tape seized by the suspect.

Although there are various types of explosives devices, as discussed in Chap. 9, some common componentry is especially important in the context of latent print analysis. One example is tape, which can be an excellent source for latent fingerprints [12]. Two common types seen in explosives cases are duct tape and electrical tape, usually wrapped around a pipe or device body. Before directing the pipe and tape to a latent print examiner, it may be necessary to consult with a trace examiner, as they may need a tape sample that has not been exposed to chemical processing (see Sect. 11.4.1). The trace examiner can also assist with looking for and collecting possible hairs and fibers from the tape during removal from the device to maximize the evidence that can be obtained from the item.

Ideally, the outer layers of tape should be processed and examined for the presence of identifiable latent prints, and then swabbed for DNA, prior to removal. There could be prints that overlap the pieces of the exposed tape that are identifiable when the tape is left in place, but after the tape is peeled off it may separate the print to the point where it is no longer of value (Fig. 11.7). The outer layers may also have been handled by other individuals between the construction of the device and receipt in the laboratory. Removing the tape and processing both the adhesive and non-adhesive sides of the protected layers should follow processing of the exterior. Any latent prints on the protected layers have an increased likelihood of being placed there by the individual that constructed the device.

As discussed in Chap. 9, pipes are often used as the container for an improvised explosive device. Metal pipes generally have threaded ends that are not good for latent prints, but are good for DNA; the smooth areas of pipes, whether metal or plastic, are a good surface for latent prints. There can be a broad variety of other components present, and each component should be assessed to determine if a latent print examination would be of value. Larger, smoother components such as batteries, present an excellent surface for the deposition of latent prints. Many

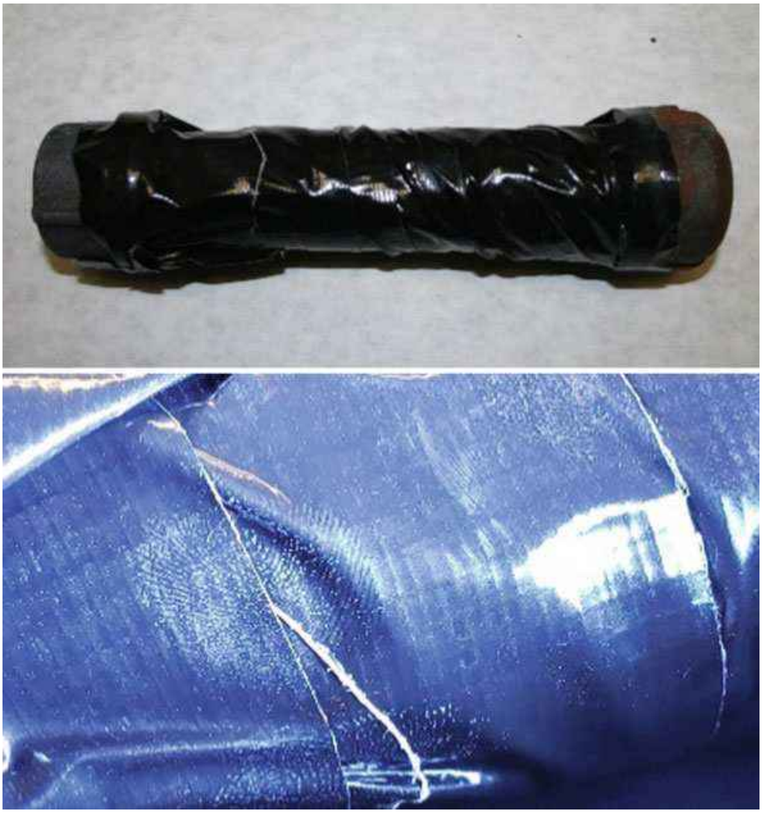


Fig. 11.7 Tape-wrapped pipe (top) with print on overlapping tape pieces (bottom)

times, wires and enhancements (discussed in Chap. 9) are too small or textured for identifiable latent prints to be present, but they can be swabbed for DNA. Especially, good areas to swab for DNA are areas of wires that have been twisted together. Thinking about how an item is normally handled is not only good for attempting to preserve latent prints, but also for DNA collection. Buttons, switches, lids, handles, levers, end caps, bodies of pipes, etc., should be swabbed for DNA as well.

11.4 Trace Evidence

Jamie Baerncopf, Forensic Chemist- Fire Debris, Bureau of Alcohol, Tobacco, Firearms, and Explosives, Forensic Science Laboratory-San Francisco.

Trace evidence constitutes a broad range of evidence types which may include tape and adhesives, fibers, hairs, paint, and other microscopic materials. Trace evidence is commonly encountered in fire and explosives investigations. An examiner conducting a fire debris or explosives examination may be cross-trained in the analysis of certain types of trace evidence. If not, they must be trained in the recognition of trace evidence even if they convene with a trace examiner for evidence collection. Great care should be used when analyzing items that may contain trace evidence as trace evidence may be easily lost. For example, incendiary and explosive devices are commonly an abundant source of evidence and should be handled in such a way as to maximize the amount of evidence recovered. Below is a discussion of different types of trace evidence that may be encountered by an examiner; however, the list is not exhaustive.

11.4.1 Tape and Adhesives

Tapes may be examined in a wide variety of contexts for fire debris or explosives examination. For example, electrical tape may be collected from a pipe bomb, duct tape may have been used to bind a victim's hands who was subsequently burned, or office tape may have been used to seal a bomb threat letter. In all of these cases, it is possible to compare a questioned tape such as that from a device or scene to another questioned tape to link evidence from different scenes or to known tape collected from a suspect. Studies have shown that there is adequate variability between brands and batches of tape and consistency within a single roll of tape to give value to such a comparison of questioned to known [13–16]. A wide variety of instrumentation is involved in a tape comparison including stereomicroscopy, polarized light microscopy (PLM), fourier transform infrared spectroscopy (FTIR), scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS), and gas chromatography-mass spectrometry (GC-MS).

At the most basic level, tapes consist of an adhesive applied to a backing. Depending on the end use, tape construction may be more complex such as the addition of fabric or fiber reinforcement in duct or filament tape. Additional levels of complexity add value to the comparison of two tapes. The backing, adhesive, and fabric reinforcement are the components of tape that are most commonly analyzed and compared. A comparison of physical and microscopical characteristics such as width, thickness, backing color, backing surface texture, and adhesive color should be done before chemical analysis (Fig. 11.8). If any of these characteristics are considerably different between a questioned and a known sample, no further analysis is required and it may be concluded that the tapes originated from different sources. If the physical characteristics are generally consistent between a questioned and a known tape, a comparison of the chemical composition, including elemental composition, will follow. If the physical characteristics and chemical composition of a questioned and known tape are consistent, it may be concluded that the two originated from the same source or another source with the same physical

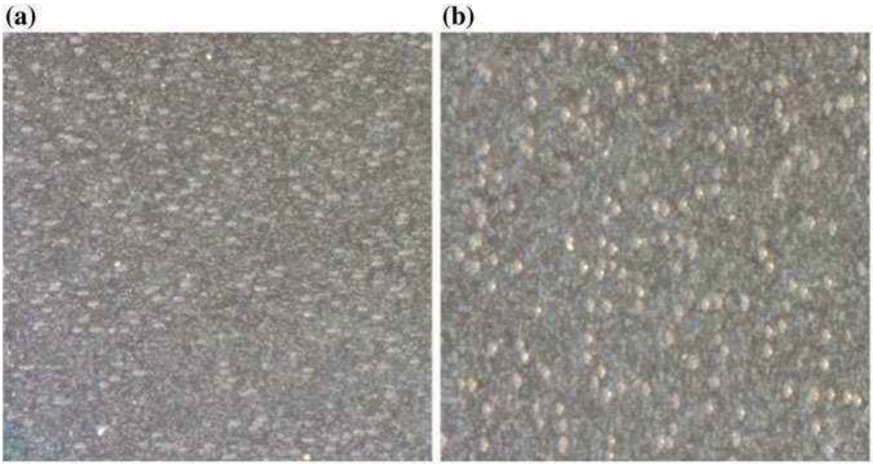


Fig. 11.8 Surface texture of the backing of an electrical tape viewed parallel (**a**) and perpendicular (**b**) to the length of the tape viewed under a stereomicroscope

characteristics and chemical composition. An examiner may not unequivocally state that a questioned and known tape originated from the same source unless a **physical fit** between the two can be made.

Typical passive headspace analysis for fire debris should not affect the examination of tape; however, the use of solvents in either a fire debris or explosives examination or latent print processing may affect the analysis. A fire debris or an explosives examiner should preserve an area of the tape for subsequent trace examination. A length of one inch encompassing the full width of the tape is ideal; however, cases are frequently far from ideal. Oftentimes with post-fire or post-blast evidence, it is difficult to find a protected area of tape for analysis. The tape may be contaminated with dirt or other material, and the tape may be burned or stretched, which may affect both chemical composition and physical characteristics. In these cases, it is generally best to consult with a trace examiner who will advise or may select their own areas for analysis.

Other adhesives may also be encountered in fire debris or explosives cases, particularly in devices where they can be used to secure fuses or other components. Analysis of these adhesives is considerably simpler than tape and generally involves identification of the type of adhesive by FTIR.

11.4.2 Hairs and Fibers

Hairs and **fibers** are a crucial piece of trace evidence as they may link an item of evidence to a person [17, 18]. A fire debris or explosives examiner should always be observant of hairs and fibers and evaluate their potential significance, even if a trace examination is not specifically requested.

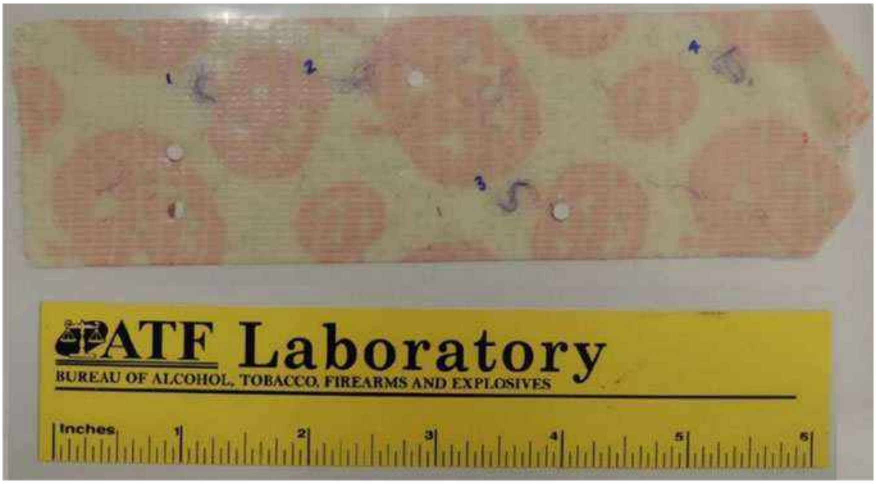


Fig. 11.9 Tufts of purple fibers of interest marked on the adhesive side of duct tape

There are innumerable places where an examiner may find hairs and fibers. Hairs or fibers collected from the clothing of a victim or suspect may indicate contact between two people. Hairs or fibers collected from a Molotov cocktail or pipe bomb may provide a valuable link to the person who constructed the device. Tape and adhesives are often great sources of trace evidence as hairs and fibers may be attached to the adhesive side of the tape or caught up in the adhesive used to attach components of a device (Fig. 11.9). However, in evaluating evidence for hairs and fibers, it is important to consider the context. When in doubt, it is often best to collect the trace evidence in case it is determined to be probative at a later time.

Ropes or cordage may be collected as evidence for comparison to fibers, such as twine used in a possible initiation system in an explosive device or rope used to bind the hands of a victim who was subsequently burned. In these cases, the structure of the cordage including construction and fiber type may be compared to that collected from a suspect. Though simpler than cordage, fishing line, or monofilament line, may also be encountered in casework. For example, a device in a case submitted to the author's laboratory included a monofilament line used as an initiation device. Monofilament line is not as complex as the construction of rope or twine, but it was still valuable to the investigation when it was determined to be consistent with the fishing line collected from the suspect's residence.

A fabric comparison may also be requested as part of a trace examination. This is common when clothing or cloth of some kind is part of an incendiary or explosive device, such as a cloth wick in a Molotov cocktail or a pipe bomb wrapped in cloth to conceal it. In a questioned fabric, there are several features for comparison to a known fabric including fiber type, knit or weave type, and overall fabric construction (Fig. 11.10). Printed fabric may also provide an additional point of comparison. Multiple cases have been submitted to the author's laboratory in which

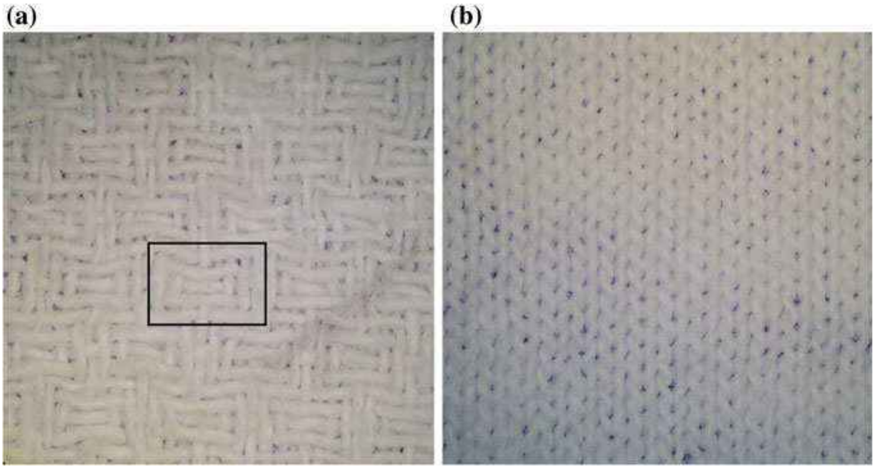


Fig. 11.10 Comparison of the construction of two white fabrics, one woven (**a**, with repeating weave pattern marked) and one knit (**b**)

investigators requested a comparison of cloth wicks from Molotov cocktails to an item recovered from a suspect's house. In one case, it was determined that, though the fiber content of the cloth wicks and curtains from a suspect's house were consistent, the construction differed so the curtains could not have been the source of the cloth wicks used in the Molotov cocktails. In another case, cloth wick with a floral pattern was physically fit to a bedsheet at a suspect's home.

Possible hairs should be collected with great care in an effort to not break or damage the hair. If a hair is broken during collection, it should be noted and the two pieces preserved together if possible. A trace examiner will determine if the hair is animal or human. If the hair is human, it can be further characterized by race and somatic origin. The gross characteristics of the hair such as the length, color, and appearance (straight, curly, etc.) can be used to determine the value of a questioned hair and may influence further analysis. For example, a comparison of a long brown hair from the scene to a suspect with short red hair is not necessary. If the gross physical properties of the hair are consistent with a person of interest, it may be possible to do a microscopical comparison of the questioned and known hairs. Typically, head and pubic hairs are microscopically compared since other body hair may lack sufficient microscopic characteristics for comparison. Microscopical comparison of hairs can be of great value to an investigation; however, it should be noted that testimony regarding the strength of associations based on hair comparisons has been discussed in recent years [19].

Hairs can also contain valuable DNA evidence. Hairs may be submitted for nuclear or mitochondrial DNA analysis. Most hairs are suitable for **mitochondrial DNA** analysis, whereas only hairs with possible tissue attached are suitable for **nuclear DNA** analysis (Fig. 11.11). Though nuclear DNA analysis is more

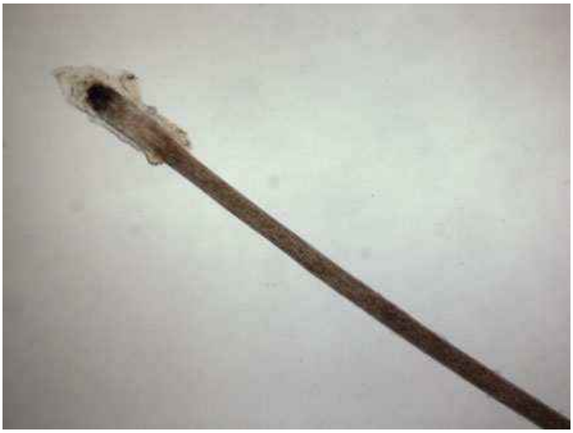


Fig. 11.11 Human hair root with tissue attached which would be suitable for nuclear DNA analysis

definitive in identifying a suspect, mitochondrial DNA can still be extremely valuable, particularly when coupled with a microscopical comparison.

Hairs and fibers may be collected and preserved in various ways. Oftentimes, hairs and fibers may be simply collected on the sticky portion of a paper sticky note, then folded over, and preserved in a small manila envelope. Alternatively, hairs, fibers, or any other trace evidence may be saved in a piece of paper folded to make a pocket or in a petri dish. With these alternate methods, the hair or fiber may be more difficult to find. Depending on the substrate, tape lifts and vacuum sweepings may also be effective methods for collecting hairs and fibers. It may be useful to communicate with a trace examiner to determine their preferred method of preservation.

11.4.3 Paints and Coatings

Examiners should also be aware of the potential value of paints and coatings as trace evidence. In fire debris and explosives casework, the examiner primarily sees architectural paint and spray paint, though automotive paint may be encountered as well. Paints/coatings may be observed on a device such as a pipe bomb or it may be observed as graffiti at a scene. In such cases, paint found on a piece of evidence, such as a device, may be compared to paint collected from a suspect, from another painted item, or from a scene. For example, spray-painted graffiti was scraped off a wall at a fire scene and compared to spray paint collected from a suspect (Fig. 11.12). The spray paints were determined to be different in physical characteristics and chemical composition.

Both physical characteristics and chemical composition of paints and coatings can be evaluated and compared [20]. Physical characteristics include color and surface features/texture. The instrumentation typically used to determine chemical

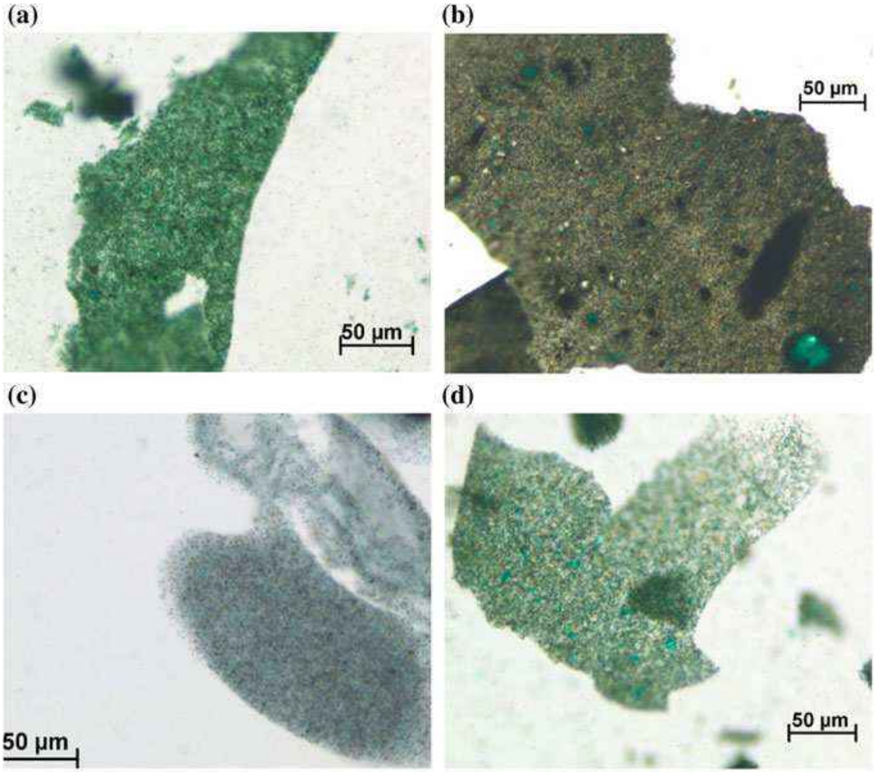


Fig. 11.12 Comparison of spray paint from graffiti at a fire scene (**a**) and spray paints recovered from a suspect (**b**–**d**)

and elemental composition includes FTIR, pyrolysis GC-MS, SEM-EDS, and PLM to identify components such as the binder, pigments, extenders, and additives.

Paints and coatings may be recovered in a number of ways. For items that have been painted, a trace examiner may prefer to examine the entire piece of evidence and collect the paint themselves. Otherwise, a fire debris or explosives examiner may scrape a sample of the paint from the item, recover a loose paint chip in a paper fold or on a post-it note, or tape lift to collect paint from an item such as clothing. In collecting paint that may contain layers, it is important that all layers are collected, down to the unpainted substrate. It should be noted that tape adhesive may interfere with the analysis of the paint [21]. The fire debris/explosives examiner should consult with a trace evidence examiner to determine if the paint evidence should be collected before beginning their analysis.

11.4.4 Other Trace Evidence

This chapter does not attempt to include all possible trace evidence that may be encountered in fire debris or explosives casework. For instance, glass and soil are common types of trace evidence that can link a victim or suspect to a scene. Though glass, soil, and other microscopic evidence may not be frequently encountered in fire debris or explosives casework, an examiner should always approach a case with an open mind and a sharp eye for any possible trace that could be probative in an investigation.

11.5 Forensic Engineering in Fire and Explosives Investigations

Jeremy Neagle, P.E, Electrical Engineer, ATF Fire Research Laboratory.

Forensic engineering applies the principles of engineering to the evaluation of materials, systems, appliances, wiring, or objects. The application of these principles, standards, and tests allows the engineer to provide an opinion of the cause of the failure or performance of the item [22].Testing may fall under one or more of many engineering disciplines. However, forensic engineering related to fire and explosives investigations typically involves electrical/electronics engineering, mechanical engineering, fire protection engineering, or structural engineering. In many fire investigations, damaged wiring or appliances will need to be examined by an electrical or mechanical engineer to determine if it was damaged as a result of the fire or was the cause of the fire. Forensic engineers may perform standardized testing and examinations through the course of their duties. However, they are typically employed to find solutions to unique investigative questions.

Forensic engineers utilize their education, training, and skills to tailor an analysis specific to the question at hand. In fire and explosives investigations, the tools used often include physical examination (including microscopy, radiography, computed tomography), electronic data recovery, materials testing, small- or full-scale testing and measurement, mathematical analysis, computer modeling, etc.

Forensic electrical engineers examine fire-damaged electrical/electronic items for evidence of failures that may have played a role in a fire's cause. This analysis may be done in the field or in the laboratory. They often survey electrical system conductors and appliance wiring for artifacts of fire-induced damage to the wires or conduct larger-scale mapping activities in an attempt to glean information about how the fire and electrical system interacted. These activities may be used to aid in the establishment of an area of fire origin, fire growth, or movement within a compartment, timeline development, or establish a sequence of events. Gaining a thorough understanding of a structure's electrical system, and how it interacted with a fire, may also yield other investigative information and should be fully exploited.

Forensic fire protection/mechanical engineers examine fire protection systems, detection, and alarm systems and analyze data from these systems to get a better understanding of the interaction of the systems with the fire. These systems may provide both physical and electronic data. Further, forensic fire protection/mechanical engineers may be engaged in testing of various fire scenarios or hypotheses, either physically, cognitively, or through the use of mathematical or computer-aided methods. Much of this work relies upon complete and accurate input data for analysis. This often requires the identification and characterization of fuel or other materials recovered from a fire scene. Generally, an analysis is only as accurate as the underlying assumptions and input data. A greater understanding of the materials involved in a fire can greatly improve the results of a test/analysis.

11.5.1 Interactions with Fire Debris and Explosives Examiners

While there is not generally as much interchange between fire debris/explosive chemists and forensic engineers as there is with the other disciplines already discussed, a symbiotic relationship between forensic chemists and forensic engineers can produce otherwise unrealized data about a given item. For example, the identification of arc melting on electrical conductors may not be possible with the tools typically available to an electrical engineer. High-level magnification or elemental analysis of an artifact may be required to accurately make a determination. SEM-EDS analysis is typically within the purview of the forensic chemist. Working together, the forensic chemist and electrical engineer can examine features such as grain structure and porosity of the metal, or identify elements such as zinc, aluminum, or iron on a copper conductor. These findings may allow a determination of arc melting versus alloying or other damages (Figs. 11.13 and 11.14).

Often, forensic engineers have access to radiography equipment, both digital radiography (X-ray) and computed tomography (CT). These tools can be invaluable to the forensic chemist during the examination of explosive devices, as they can be utilized to identify items not otherwise visible to the examiner. This includes items within the containment of the device, beneath or within layers of tape, glue or other adhesives, etc. Items of trace evidence may be revealed by separating materials by density and thickness using a CT scanner prior to disassembly of the item.

Electrical/electronics engineers often have a vast knowledge of electrical/electronic components and can be a useful resource for the forensic chemist in identifying items recovered from an explosive device or post-blast scene. The engineer's knowledge may assist in identifying explosive device components, either by manufacturer/model, type/function of component, or the source of the component where items have been harvested from other products to construct the device. With post-blast debris, forensic engineers can also be useful in differentiating items, which may be from device components versus other items found at the

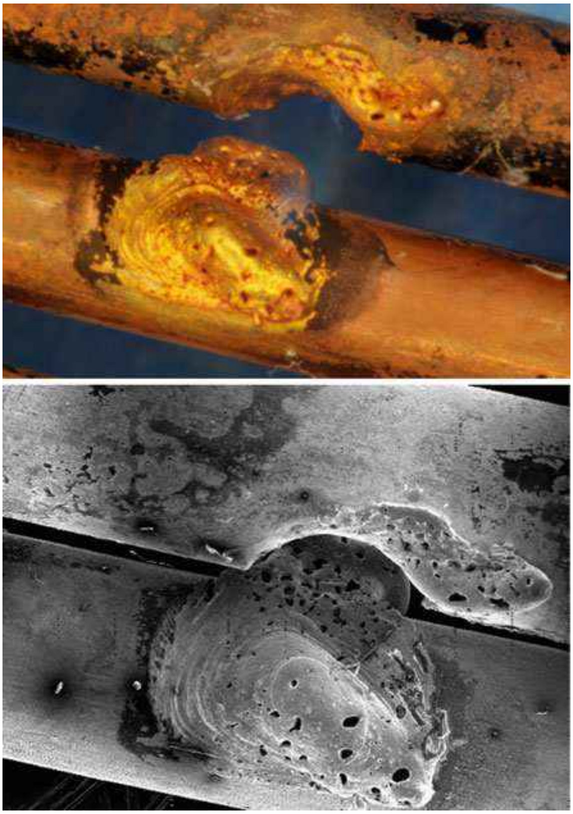


Fig. 11.13 Microscope image (top) and SEM image (bottom) of arc melting on copper wire [23]

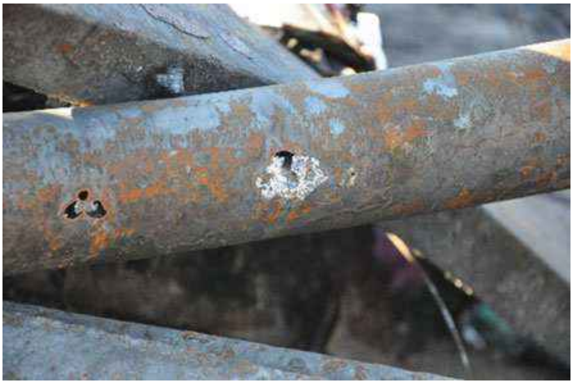


Fig. 11.14 Image of a hole formed by alloying of steel conduit and aluminum wire

scene (e.g., separating device components of a vehicle-borne explosive device from vehicle components).

Electrical/electronics engineers may also be utilized to assist with the development of incendiary and explosive device circuits and schematic diagrams. Further, they may be able to analyze or test the circuit for operation or functionality. Lastly, they may be able to examine device components to determine if the components have been modified or tampered with.

Fire protection engineers may conduct fire tests or perform computer fire modeling to test hypotheses related to a fire, or to study a particular fire scenario. Exemplar or test materials are often used to represent those found at the scene. While engineers may have the majority of equipment necessary to quantify and compare exemplar or test materials to materials recovered from the scene, a forensic chemist is often relied upon to provide information about these materials. For example, a trace chemist may be needed to identify and compare carpet materials or to examine fabrics to determine the type or blend of fibers.

While forensic engineers and chemists may work independently, there are times when the work of one may impact the other. In these situations, careful coordination is required to ensure that the objectives of both disciplines are met. Much of a forensic engineer's work relies on non-destructive testing (NDT) techniques. However, often items must be carefully disassembled during the examination process to identify potential failures or further study the item. It is generally preferred for other forensic disciplines (including fire debris/explosive chemists, trace chemists, DNA, latent print and toolmark examiners) to perform their work first so that trace evidence is not disturbed during the forensic engineering examination.

While carrying out their examinations, forensic examiners should consider any potential impact that their examinations may have the subsequent work of a forensic engineer. This may require increased awareness when multiple forensic disciplines are involved and items of evidence are passed between examiners.

Passive headspace concentration for fire debris analysis does not alter the physical characteristics of the evidence and should not affect the forensic engineer's examination. An explosive chemist's work is typically much more invasive and may alter items of evidence. Device components may be disassembled in an attempt to collect explosive material or residue samples, to identify device components, or to recover items of trace evidence. In these cases, if a forensic engineering examination is to be conducted, it is generally best to consult with the forensic engineer to formulate an examination plan that yields the best result. It is also advisable to extensively document and photograph any assembly as received before disassembly begins, as the original configuration is typically very important for the forensic engineer and may not be immediately intuitive. Additionally, documenting each step of the disassembly is critically important to capture any mechanical components which were not documented on the initial observations.

11.6 Integrating Fire and Explosives Analysis with Other Forensic Disciplines

Carl E. Chasteen, BS, CPM, FABC, Chief of Forensic Services, Bureau of Forensic Services, Division of Investigative and Forensic Services, Department of Financial Services, State of Florida.

For fire debris and explosives examiners, the required extractions and device deconstruction for explosives and ignitable liquid residues could potentially compromise future examinations by the other disciplines. A decision must be made as to which type of evidence analysis will potentially provide the most information. This 'choice' has been referred to as the 'best evidence' choice or 'conundrum.' Rarely is there a perfect schema or plan. Examiners and laboratories are encouraged to give this issue consideration in advance and in conjunction with other disciplines, where possible. Some samples are potentially delicate and may not survive a fire or explosion and may not survive the required extraction processes for ignitable liquids and explosives. Depending on the nature of the sample, the fire, heat, or pressure wave may cause the evidence to char, or warp, or deform to a degree where the suppression and overhaul activities of the fire department will render it unusable for any forensic analysis other than for ignitable liquid or explosives residues. There will, however, be occasions when the scene investigator will identify evidence samples and submit them for additional forensic analyses as well as ignitable liquid residues or explosives residues analyses. The examiner needs to be able to look at these items and assess if other forensic disciplines may be useful.

The initial problem faced by the fire debris or explosives examiner is that the sample has typically come from a scene where it has become moist and has been placed inside a sealed airtight container. This becomes an ideal medium for the growth of mold or certain bacteria which may potentially destroy or alter any organic-based evidence so that other forensic analyses are not possible. As with the other moisture-sensitive disciplines discussed earlier, one possible method of handling this problem is expedited analysis for ignitable liquids, followed by drying of the sample.

To demonstrate the considerations and analytical flow that is possible in a laboratory, consider a standard Molotov cocktail. As discussed in Chap. 2, a Molotov cocktail generally consists of a breakable container, some type of wick, and ignitable liquid. For the sake of this example, the Molotov cocktail in question consists of a glass bottle with a cloth wick and an ignitable liquid. The first consideration that an examiner has is the appropriate examinations that can be conducted for each portion of the evidence. For the ignitable liquid sample, only one analysis is possible (ignitable liquid), but for the cloth wick and the bottle, other examinations are possible. The cloth may have DNA and trace evidence, in addition to ignitable liquid analysis. Both of these examinations could be conducted after the ignitable liquid analysis, the former after the cloth has been dried. The bottle is potentially viable for latent print and DNA evidence.

Once the examiner has determined what examinations are possible, they can then consult the accompanying case information or the submitter to determine if these examinations are probative, or if there is a reason that they may not have been requested. By determining the possible examinations at the beginning of analysis, however, the examiner can avoid inadvertently voiding later examinations.

11.7 Questions

1. Discuss how heat, flame, or pressure waves could interfere with additional analysis of the evidence by other forensic disciplines.
2. Discuss potential issues for other examination types when vapor-tight packaging for FD or e-evidence is used.
3. How do explosives or fire debris examinations affect DNA analysis? What can be done to limit these effects?
4. Why are latent prints on non-porous surfaces particularly susceptible to damage?
5. An exploded pipe bomb partially wrapped in tape is submitted to the laboratory for examination. What can an explosives examiner do to preserve the potential for latent print processing? For tape comparison?
6. Can a comparison ever unequivocally link tape from a device to a known roll of tape?
7. Describe types of trace evidence that a fire debris/explosives examiner should be cognizant of during their examination.
8. What type of DNA testing is possible from a collected hair?
9. What are typical examinations performed by forensic engineers? What steps should an examiner take to preserve evidence that may be evaluated by a forensic engineer?

References

1. Elsayed ASI et al (2015) DNA Fragmentation and apoptosis caused by gasoline inhalation, and the protective role of green tea and curcumin. Pyrex J Biomedical Research 1:68–73
2. Tontarski KL, Hoskins KA, Watkins TG, Brun-Conti L, Michaud AL (2009) Chemical enhancement techniques of bloodstain patterns and DNA recovery after fire exposure. J For Sci 54:37–48
3. Raymond JJ, van Oorschot RA, Gunn PR, Walsh SJ, Roux C (2009) Trace evidence characteristics of DNA: a preliminary investigation of the persistence of DNA at crime scenes. Forensic Sci Int Genetics 4:26–33
4. Karni M, Zidon D, Polak P, Zalevsky Z, Shefi O (2013) Thermal degradation of DNA. DNA Cell Bio 32:1–4
5. Champod C, Lennard C, Margot P, Stoilovic M (2004) Fingerprints and other ridge skin impressions. CRC Press, Boca Raton

6. Yamashita B, French M, et al. The fingerprint sourcebook, Latent print development, Chapter 7. https://www.ncjrs.gov/pdffiles1/nij/225327.pdf
7. Stow KM, McGurry J (2006) The recovery of finger marks from soot-covered glass fire debris. Sci Justice 46:3–14
8. Bradshaw G, Bleay S, Deans J, NicDaeid N (2008) Recovery of fingerprints from arson scenes: Part 1—latent fingerprints. J Forensic Ident 58:54–82
9. Lounsbury DA, Thompson LF (2006) Concerns when using examination gloves at the crime scene. J Forensic Ident 56:179–183
10. Hall MM (1991) Ridge detail through latex gloves. J Forensic Ident 41:415–416
11. Yamashita B, French M, et al. The fingerprint sourcebook, Latent print development, Chapter 7, pp 14–22, https://www.ncjrs.gov/pdffiles1/nij/225327.pdf
12. Champod C, Lennard C, Margot P, Stoilovic M (2004) Fingerprints and other ridge skin impressions. CRC Press, Boca Raton, p 160
13. Smith, JM (2007) Forensic examination of pressure sensitive tape. In: Blackledge, RD (ed) Forensic analysis on the cutting edge. Wiley, pp 291–332
14. Smith J (1998) The forensic value of duct tape comparisons. Midwestern Assoc Forensic Scientists Newsl 27(1):28–33
15. Mehltretter AH, Bradley MJ, Wright DM (2011) Analysis and discrimination of electrical tapes: part I. adhesives. J Forensic Sci 56:82–94
16. Mehltretter AH, Bradley MJ, Wright DM (2011) Analysis and discrimination of electrical tapes: part II: backings. J Forensic Sci 56:1493–1504
17. Robertson J, Roux C, Wiggins KG (2017) Forensic examination of fibres, 3rd edn. CRC Press, Boca Raton
18. Bisbing, RE (2002) The forensic identification and association of human hair. In: Saferstein R (ed) Forensic science handbook, vol 1, 2nd edn. Pearson, Upper Saddle River, pp 389–428
19. FBI Press Release (2015) FBI testimony on microscopical hair analysis contained errors in at least 90 percent of cases in ongoing review. https://www.fbi.gov/news/pressrel/press-releases/fbi-testimony-on-microscopic-hair-analysis-contained-errors-in-at-least-90-percent-of-cases-in-ongoing-review
20. Thornton JI (2002) Forensic paint examination. In: Saferstein R (ed) Forensic science handbook, vol 1, 2nd edn. Pearson, Upper Saddle River, pp 429–452
21. Scientific Working Group on Materials Analysis (1999) Forensic paint analysis and comparison guidelines. Forensic Sci Commun 1(2). https://archives.fbi.gov/archives/about-us/lab/forensic-science-communications/fsc/july1999/painta.htm
22. American Society of Civil Engineers (2018) Forensic engineering. https://www.asce.org/forensic-engineering/forensic-engineering/. Accessed 15 Jun 2018
23. Novak C (2011) An analysis of heat flux-induced arc formation in residential electrical cables. Thesis, University of Maryland, College Park

Carl Chasteen is the Chief of Forensic Services within the Division of Investigative and Forensic Services for the Florida Department of Financial Services and has managed the forensic laboratory since 1992. Prior to that, he was an analyst with in the Ohio Fire Marshal's Forensic Laboratory. Carl Chasteen specializes in fire debris and explosives analysis, and has developed and taught classes in fire debris analysis for the National Center for Forensic Science at the University of Central Florida. He also helped to develop the National Fire Academy Fire Investigation: Forensic Evidence course (#R214) and has taught the class many times.

Appendix A
Acronyms and Abbreviations

2,4-DNT	2,4-Dinitrotoluene
ABS	Acrylonitrile butadiene styrene.
AN	Ammonium nitrate
ANFO	Ammonium nitrate/fuel oil
APCI	Atmospheric pressure chemical ionization
AQAP	Al-Qaeda in the Arabian Peninsula
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflectance
AWG	American wire gauge
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
C18	Octadecane
CCD	Charge-coupled detector
CE	Capillary electrophoresis
CI	Chemical ionization
CID	Collision-induced dissociation
CPVC	Chlorinated polyvinyl chloride
CT	Computed tomography
DAD	Diode array detector
DART	Direct analysis in real time
DCDA	Dicyandiamide
DDT	Supersonic detonation
DESI	Desorption electrospray ionization
DMDNB	2,3-Dimethyl-2,3-dinitrobutane
DPA	Diphenylamine
DWV	Drainage, waste, and vent
ECD	Electron capture detector
EDS	Energy-dispersive spectroscopy
EDXRF	Energy-dispersive X-ray fluorescence
EGDN	Ethylene glycol dinitrate

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4

EI	Electron ionization
EIP	Extracted ion profile
EOD	Explosives ordnance disposal
ESI	Electrospray ionization
ETN	Erythritol tetranitrate
eV	Electron volt
FA	Fatty acid
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FID	Flame ionization detector
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GC-ECD	Gas chromatography with electron capture detector
GC-FID	Gas chromatography with flame ionization detector
GC-MS	Gas chromatography–mass spectrometry
GSR	Gunshot residue
H	Plate height
HETP	Height equivalent to theoretical plate
HME	Homemade explosive
HMTD	Hexamethylene triperoxide diamine
HPD	Heavy petroleum distillate
HPLC	High-performance liquid chromatography
HTGC-MS	High-temperature gas chromatography–mass spectrometry
HTH	Calcium hypochlorite
IC	Ion chromatography
IC-MS	Ion chromatography–mass spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
IEC	Ion exchange chromatography
IED	Improvised explosive device
ILR	Ignitable liquid residue
ILRC	Ignitable Liquid Reference Database
IMS	Ion-mobility spectrometry
IST	Ignition susceptibility test
LC	Liquid chromatography
LC-MS	Liquid chromatography–mass spectrometry
LIMS	Laboratory information system
LPD	Light petroleum distillate
m/z	Mass-to-charge ratio
MMAN	Monomethylamine nitrate
MPD	Medium petroleum distillate
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
N	Theoretical plate
NAA	Neutron activation analysis
NAD+	Nicotinamide adenine dinucleotide

NC	Nitrocellulose
NDT	Nondestructive testing
NFPA	National Fire Protection Association
NG	Nitroglycerin
NICI	Negative ion chemical ionization
NM	Nitromethane
NMR	Nuclear magnetic resonance
NP	Naphthenic–paraffinic products
NQ	Nitroguanidine
NSF	National Sanitation Foundation
PBX	Polymer-bonded explosive
PDA	Photodiode array
PDF	Powder Diffraction File
PDMS	Polydimethylsiloxane
PETN	Pentaerythritol tetranitrate
PHC	Passive headspace concentration
PIES	Power switch, initiator, explosive, and switch
PLM	Polarized light microscopy
PNA	Polynuclear aromatic
PUFA	Polyunsaturated fatty acid
PVA	Polyvinyl alcohol
PVC	Poly(vinyl chloride)
QC	Quality control
QqQ	Triple quadrupole mass analyzer
rf	Radio frequency voltage
Rf	Retention factor
SEM	Scanning electron microscope
SEM-EDS	Scanning electron microscope–energy-dispersive spectroscopy
SOP	Standard operating procedure
SPE	Solid-phase extraction
SPICE	Switch, power source, initiator, container, explosive
SPME	Solid-phase microextraction
STR	Short tandem repeat
SVO	Straight run vegetable oil
T/SWGFEX	Technical and Scientific Working Group for Fire and Explosion Analysis
TAG	Triacylglyceride
TATP	Triacetone peroxide
TEA	Chemiluminescence thermal energy analyzer
TIC	Total ion chromatogram
TLC	Thin-layer chromatography
TNT	Trinitrotoluene
TOF	Time of flight
tr	Retention time
UL	Underwriters Laboratories

UPLC	Ultra-high-pressure liquid chromatography
UVS	Ultraviolet spectrophotometry
VO	Vegetable oil
VOC	Volatile organic compound
VOD	Velocity of detonation
VOR	Vegetable oil residue
XRD	X-ray diffraction
XRF	X-ray fluorescence

Appendix B
Answers to Chapter Questions

Chapter 1

Question 1.2

While the characteristics for NAA in forensic analysis are quite promising, the technique is very expensive and impractical for a forensic laboratory.

Question 1.3

In a split injection, only a fraction of the gaseous sample in the inlet is injected into the column and the remainder is flushed out of the inlet by the split flow. In a splitless injection, the split flow is turned off briefly to allow most of the sample to enter the column. For routine analysis, split flows yield better peak shapes and separations by avoiding overloading the capillary column. When high sensitivity is required for small amounts of analyte, a splitless injection might be useful.

Question 1.4

(a) This is the unretained pentane solvent.
(b) If we estimate a retention time of 18.5 min based on the data, the oven temperature would be 205 °C based on the temperature program.
(c) Likely an FID or a GC-MS with an EI source. ECD would not be appropriate because it is insensitive to alkanes.

© Springer Nature Switzerland AG 2019

K. Evans-Nguyen and K. Hutches (eds.), *Forensic Analysis of Fire Debris and Explosives*, https://doi.org/10.1007/978-3-030-25834-4

Question 1.5

While components of the atmosphere do not absorb significantly in the UV–Vis region, CO_2 and water vapor absorb in the IR very well. The resulting high IR background must be accounted for through subtraction to obtain usable spectra.

Question 1.7

The top spectrum was acquired using negative mode CI. The base peak is the $[M - H]^-$ peak representing the intact molecule. The bottom spectrum does not have the molecular ion (*m/z* 227) as the base peak and displays significantly more fragmentation. The base peak at *m/z* 227 represents the commonly observed $[M - OH]^-$ ion.

Chapter 2

Question 2.1

Evidence for fire debris analysis needs to be packaged in vapor-tight packaging such as cans, fire debris bags, or jars.

Question 2.2

Ignitable liquids are classified rather than brand identified because an ignitable liquid from a single class may be marketed and sold as different commercial products.

Question 2.3

The overall goal of a petroleum refinery is to transform crude oil into the maximum amount of profitable fuel using chemical and physical means.

Question 2.4

Ignitable liquids are classified based on chemical composition and boiling point range.

Question 2.5

Data interpretation involves pattern recognition, in which characteristic petroleum patterns are noted in the data, and pattern comparison, in which the patterns are compared to a known ignitable liquid.

Question 2.6

Comparison samples are samples of household substrates that are believed to be free of ignitable liquids. Comparison samples may help determine if a substrate being examined, such as flooring or carpet, inherently contains an ignitable liquid.

Question 2.7

Lubricating oils are included in fire debris analysis because they are typically petroleum products. Vegetable oils are also included in fire debris analysis because they may be subjected to spontaneous heating and cause a fire.

Question 2.8

An incendiary device is a device that is designed to start or communicate a fire. If the Molotov cocktail is intact, a sample of liquid should be removed from the bottle for ignitable liquid analysis. The remaining liquid in the bottle can be discarded and the bottle dried and packaged for fingerprints and DNA. The wick of the Molotov may then be packaged in a can to preserve any ignitable liquids. If the Molotov cocktail has been deployed, the fragments of glass and wick should be packaged separately in vapor-tight packaging to avoid contact between the glass and the wick which may impact the recovery of DNA or fingerprints.

Question 2.9

Examiners should avoid terms like “arson” or “accelerant” because they are biasing and imply intent. Examiners should remain objective and unbiased.

Chapter 3

Question 3.1

Pyrolysis, combustion, and distillation.

Pyrolysis is a chemical reaction caused by the application of thermal energy (heat) in the absence of oxygen where larger molecules are broken down into smaller ones.

Combustion is the thermal reaction of organic compounds in the presence of oxygen, which under ideal conditions will produce only carbon dioxide and water; however, incomplete combustion results in the formation of new compounds. Combustion may also be thought of as "oxidative pyrolysis."

Distillation is the process, whereby volatile organic compounds are released or extracted from a material by the application of heat; for example, the release of various terpenes from burning softwood results from distillation.

Question 3.2

Monomer reversion, random chain scission, and side group scission.

Question 3.3

Polyethylene is a common thermoplastic used to manufacture many different types of materials, and so its thermal degradation products will often be encountered in samples of fire debris. Polyethylene undergoes random chain scission during pyrolysis to almost exclusively generate a homologous series of triplets typically over the carbon range C_8–C_{20} and higher. Each triplet is comprised of the diene, alkene, and alkane having the same number of carbon atoms where the alkene is the dominant product in each triplet. The homologous series of short-chain hydrocarbons produced by the pyrolysis of polyethylene can not only mimic a petroleum distillate but, when in high concentration, easily mask the peaks from an ignitable liquid in a chromatogram. Recognition of the diagnostic triplet pattern produced by thermal degradation of polyethylene will prevent misidentification of these degradation products as a petroleum distillate. The use of extracted ion profiles will assist in confirming the presence of an underlying ignitable liquid if the total ion chromatogram is dominated (masked) by the degradation products of polyethylene.

Question 3.4

The combustion of body tissue is often limited to the exterior surface which is predominantly subcutaneous fat.

Question 3.5

The main pyrolysis/combustion products from fat are a homologous series of n-alkanes (C9–C13), n-alkenes (C7–C13), and n-aldehydes (C5–C10), plus some dienes (C10–C12).

Question 3.6

Residual solvents (ignitable liquid) may be present as part of the manufacturing process and subsequently detected during routine fire debris analysis. Not all ignitable liquids found in a sample necessarily indicate that an ignitable liquid was brought to the scene by an arsonist. For example, a medium petroleum distillate may be indigenous to the scene if the fire debris sample was a piece of wood from a recently stained deck, or the presence of toluene in a pair of running shoes from the suspect is likely from the adhesive used at the factory to glue the shoe together.

Question 3.7

Three examples from the text are provided:

1. Residual solvent used in the manufacture of vinyl sheet flooring has been reported to contain either an isoparaffinic (i.e., Isopar H®) or a normal paraffinic (Norpar®) solvent.
2. Aftermarket products applied by consumers may also result in residual solvent being present at a fire scene. For example, exterior waterproofing products, or “sealers,” applied to concrete or wood will have detectable amounts of carrier solvent—in this case a medium petroleum distillate—for up to one month after application.
3. Solvents used in coatings designed for interior application, such as wood floor stain or polyurethane sealer, may persist for much longer periods of time.

Chapter 4

Question 4.1

True.

Question 4.2

No. Only drying oils can form hard films, which makes them valuable additives for stains, surface oils, and printing inks.

Question 4.3

No. Autoignition is where radiant heat of surrounding objects causes a material to rise in temperature to the point where it catches on fire. Spontaneous ignition is where the self-heating properties of a material cause the support medium to autoignite.

Question 4.4

No. The boiling points of FAs are too high to allow for efficient recovery using passive headspace. Biodiesel, on the other hand, has derivatized FAs that are more volatile and therefore can be recovered by passive headspace concentration.

Question 4.5

Base-catalyzed transesterification is the most common method for creating FAMEs.

Question 4.6

Animal fats, vegetable oils, used/recycled oils, and microorganisms such as algae, fungi, bacteria, molds, and yeasts.

Question 4.7

No. Ethanol elutes before most solvents. When used to analyze E85 liquids, only the gasoline portion will be detectable.

Chapter 5

Question 5.1

Source of crude oil, petroleum-refining processes, distribution system, comingling at storage site, and blending to meet product specifications.

Question 5.2

Oxygenated solvents and miscellaneous.

Question 5.3

The criteria for oxygenated solvents require the presence of a major oxygenated compound only and may include many other types of compounds. Miscellaneous ignitable liquids do not meet the requirements of the other classes and are a kind of catchall.

Question 5.4

Branched alkanes, normal alkanes, and aromatic compounds.

Question 5.5

Normal alkane products.

Question 5.6

Chromatographic patterns are simple with good peak resolution in the light carbon range, but become more complex with less peak resolution as the carbon range increases. There are more branched compounds to detect in the higher carbon ranges, which are not easily resolved. Both classes of ignitable liquids meet the broad specifications of the product.

Question 5.7

Alkane compounds are the most variable components of gasoline, as displayed in the wide range of alkane EIP responses.

Question 5.8

If the specification sheet for a given product does not have a chemical composition component, the chemical composition can vary. For instance, a product to be marketed as a brush cleaner may have on its specification sheet that the product be comprised of 90% petroleum product and 10% oxygenate with a flash point over 105 °F. The "petroleum product" content can be satisfied by either a (flash point) appropriate distillate, dearomatized distillate, isoparaffinic product, naphthenic–paraffinic product, aromatic product or a normal alkane product. Similarly, the oxygenate content can be satisfied with carbitol, butyl carbitol, a blend of carbitols, or a wide range of other oxygenated chemicals. If the specification sheet is specific as to the type of petroleum product (e.g., isoparaffinic product), then there will be less batch to batch variability in the product (both chemically and performance base).

Chapter 6

Question 6.1

Soil, wet and molding debris, any substrate with an adequate microbial community.

Question 6.2

Evidence handling: If sample descriptions on the intake forms indicate soil samples, the examiner should make sure that the evidence is kept cold and increase the priority of the case to make sure it is examined quickly before further degradation can occur. Data analysis: If a pattern does not look quite right, but only a particular type of compound is absent (i.e., n-alkanes), the examiner may be able to compare to a degraded sample or use a comparison sample. This may allow identification of an otherwise non-identifiable pattern.

Question 6.3

Compounds: Normal alkanes and monosubstituted aromatics. Classes: Gasoline, petroleum distillates.

Question 6.4

Chill/freeze: Simplest and effective at slowing degradation; it requires refrigerator/freezer space, quick and correct storage on collection, and ingenuity when no space is available.

Oxygen-absorbing pouches: Also simple and potentially effective; not extensively studied yet; and potential for contamination since something is being added to the evidence; it requires that enough pouches are available for each item being taken.

Triclosan kills microbes rather than simply slowing metabolism; is effective; and requires large volumes of pre-made solution that must be carried to scenes or applied quickly on return, potential for contamination since something is being added to the evidence, potential for can rusting due to extensive moisture within container.

Question 6.5

Weathering: Evaporation, which results in losses based on volatility. Intra-group ratios largely maintained.

Microbial degradation: Metabolism of certain classes of compounds based on microbial consumption, with loss of intra-group ratios.

Chapter 7

Question 7.1

An intact explosive can be thought of as unreacted energetic material, e.g., an intact stick of dynamite or the contents of an unfired firework. The characteristic appearance will not have changed significantly, and the original ingredients will be present.

Question 7.2

Low explosives are usually a mixture of an oxidizer and a fuel that deflagrate when initiated, meaning that the reaction through the substance occurs at a rate less than the speed of sound in the unreacted material. Examples of low explosives are black powder and smokeless powder.

Question 7.3

Black powder contains potassium nitrate, charcoal, and sulfur. Carry out a burn test; the powder should burn quickly with a yellow/lilac flame with lots of smoke generation. Identify the elements N, O, S, and C by SEM-EDS. Potassium nitrate and sulfur can be confirmed by XRD. Confirm the presence of sulfur using Raman or a chemical spot test.

Question 7.4

The principal component of all smokeless powders is nitrocellulose. Single-base smokeless powder contains nitrocellulose (NC); double base contains NC and nitroglycerin (NG); triple base contains NC, NG, and nitroguanidine (NQ).

Question 7.5

Analyze by FTIR and XRD for potassium perchlorate. XRD, SEM-EDS, Raman, or chemical spot tests will show the presence of sulfur. XRD, XRF, or SEM-EDS will identify the aluminum. The mixture is called flash powder.

Question 7.6

The three categories are primary, secondary, and tertiary high explosives. Primary explosives initiate easily without much stimuli, for example lead azide and HMTD. Secondary explosives including composition C4 and dynamite require a shock wave from a detonator to initiate. Tertiary explosives such as ANFO and emulsions usually require a shock wave from a detonator and a booster charge to initiate.

Question 7.7

Molecular high explosives are single molecules that contain their oxidizer and fuel chemically bound in one molecule. See Fig. 7.7 for example structures.

Question 7.8

Dynamites can be packaged in polyethylene evidence bags or glass vials. Dynamites that require vapor sampling should be submitted in vapor-tight packaging such as a nylon bag.

Question 7.9

Presumptive tests do not yield a conclusive identification of a material. They give an indication only but can help direct the examiner along the most appropriate analysis path. The most commonly used are the burn test (also known as ignition susceptibility test) and chemical spot tests.

Question 7.10

The characteristic appearance including morphology, color, shape, and texture and the presence of nitrocellulose are sufficient to identify a powder as smokeless powder.

Question 7.11

The FTIR spectra of NC and NG are similar and can make it difficult to identify both components in a single spectrum. They can be isolated by liquid–liquid extraction and then analyzed and identified separately by FTIR. Nitrocellulose is soluble in acetone but not dichloromethane, and nitroglycerin is soluble in both. As such, a dichloromethane rinse of a dissolved and re-solidified smokeless powder particle can effectively separate the two components.

Question 7.12

The material will have the characteristic appearance of an emulsion explosive, a dense material with the consistency of “cream cheese,” when compared with photographs or the laboratory reference collection of explosives. A microscopic examination should reveal the presence of suspended white particles (nitrate oxidizer) throughout the material. A sausage shape to the intact material may also be an indicator. With some or all of these physical features, the examiner will conclude that it is likely an emulsion explosive. The suspected emulsion can then be differentiated from water gels and slurries by chemical analysis. The most useful techniques available in this particular laboratory are XRD, FTIR, and SEM-EDX that can be used to identify the major components suspended ammonium nitrate (and/or sodium nitrate) in powder or prill form and various fuels (e.g., metal flakes) and sensitizers (e.g., microballoons).

Chapter 8

Question 8.1

- Clothing and gloves must be changed before sampling other post-blast or search scenes.
- Collection tools such as tweezers, shovels, and brushes should be disposable or cleaned between items gathered.
- Unused swabbing material from the same lot or batch used for evidence collection should be packaged on scene and submitted as control samples in similar packaging. If a solvent is used to wet the swab material before collection, the control swab should be treated in a similar fashion.

Question 8.2

SEM-EDS and XRD.

Question 8.3

Method blanks and control samples allow the examiner to monitor for possible contamination and inherent ions from supplies used during the preparation of extracts.

Question 8.4

DNT or TNT.

Question 8.5

Post-combustion black powder.

Question 8.6

Acetone and dichloromethane.

Question 8.7

Any retained water extract can be analyzed using IC-MS.

Question 8.8

To determine whether the products present in the data are indicative of an explosive, particularly for potential inorganic explosives.

Chapter 9

Question 9.1

Power source (9V battery), conductor (wire), load (detonator), switch (push button switch).

Question 9.2

Segregation, recognition, identification, function determination, comparison.

Question 9.3

Backpack for concealment, and screws or propane bottle for enhancement.

Question 9.4

No. Device analysis does not typically lend itself to definitive associations. The most that can be said is componentry that was found consistent with components used in the explosive device.

Chapter 10

Question 10.1

Cross-disciplinary cases are considered to be those that require examinations in multiple disciplines. For the purposes of this chapter, it will refer to evidence needing both ignitable liquid and explosive testing.

Question 10.2

A few examples include: ammonium nitrate and fuel oil (ANFO), ammonium nitrate and nitromethane, ammonium nitrate and nitrobenzene, potassium chlorate and mineral oil.

Question 10.3

Incendiary mixtures are materials that will cause a fire or a thermal event instead of an explosion.

Question 10.4

A hypergolic mixture consists of two or more materials that will ignite when mixed without an external ignition source. Examples include brake fluid and pool chlorinator; potassium permanganate and glycerin; and potassium chlorate, sugar, and sulfuric acid.

Question 10.5

Acceptable answers include (but are not limited to):

Exhibit 1 contained residues indicative of a mixture of chlorate, sulfuric acid, and sucrose.

Sulfate ions, chlorate ions, and sucrose were identified in Exhibit 1, which is consistent with a mixture of sulfuric acid, chlorate, and sugar.

Question 10.6

The first step would be to perform passive headspace concentration to determine if ignitable liquids or organic high explosives are present. Following this analysis, the evidence should be visually examined for potential explosive damage and residue.

Question 10.7

Potassium chloride and strontium carbonate are indicative of residues from a post-burn road flare.

Question 10.8

Instrumental methods that provide an identification of compounds, as opposed to ions or elements only, are preferable, since ions or elements alone may not be able to provide information on the original configuration of the compound.

Chapter 11

Question 11.1

Flames and pressure waves generally can (DNA, fingerprints, trace) or degrade it (toolmarks, depending on substrate, consume/melt wiring).

Question 11.2

Possible degradation of DNA; FD bags can cause rubbing of smooth surfaces, losing latent prints; ferrous tools can rust, potentially degrading the tool for later toolmark analysis.

Question 11.3

Solvent extracts can rinse away DNA; excessive handling can remove or introduce DNA; headspace techniques for FD can be used to avoid this, careful handling to avoid potential DNA-rich sites, pre-swabbing when possible.

Question 11.4

Latent prints on non-porous surfaces are susceptible to damage because they are resting on the surface of the item, instead of being absorbed into it.

Question 11.5

The item should be minimally handled in areas not expected to have been handled, with care taken not to handle the tape. A sample of the tape should be preserved before latent print processing, if possible, to preserve the ends for comparison.

Question 11.6

If the ends are compared and physically fit, then an unequivocal link can be made.

Question 11.7

Hairs, fibers (depending on the substrate), tape, etc.

Question 11.8

mtDNA if no root or a root with no tissue, and nDNA if a root with tissue attached.

Question 11.9

Examination of wiring/appliances to see if energized at the time of the fire, fire modeling/timeline development, and ignition scenario testing, and to preserve wiring, minimal handling when possible, and careful documentation.